University of New Hampshire
University of New Hampshire Scholars' Repository

Doctoral Dissertations | Student Scholarship

Fall 1994

Measurements of foliar chemistry using laboratory and airborne high spectral resolution visible and infrared data

Mary Elizabeth Martin
University of New Hampshire, Durham

Follow this and additional works at: https://scholars.unh.edu/dissertation

Recommended Citation
Martin, Mary Elizabeth, "Measurements of foliar chemistry using laboratory and airborne high spectral resolution visible and infrared data" (1994). *Doctoral Dissertations*. 1804.
https://scholars.unh.edu/dissertation/1804

This Dissertation is brought to you for free and open access by the Student Scholarship at University of New Hampshire Scholars' Repository. It has been accepted for inclusion in Doctoral Dissertations by an authorized administrator of University of New Hampshire Scholars' Repository. For more information, please contact nicole.hentz@unh.edu.

INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each original is also photographed in one exposure and is included in reduced form at the back of the book.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

UMI

A Bell & Howell Information Company
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
313/761-4700 800/521-0600

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Order Number 9511208

Measurements of foliar chemistry using laboratory and airborne high spectral resolution visible and infrared data

Martin, Mary Elizabeth, Ph.D.

University of New Hampshire, 1994

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

MEASUREMENTS OF FOLIAR CHEMISTRY USING LABORATORY AND AIRBORNE HIGH SPECTRAL RESOLUTION VISIBLE AND INFRARED DATA

BY

Mary E. Martin

B.S., University of New Hampshire (1988)

DISSERTATION

Submitted to the University of New Hampshire
in partial fulfillment of
the requirements for the degree of

Doctor of Philosophy

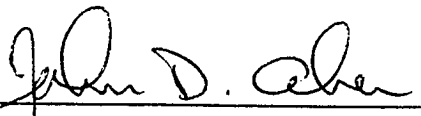
in

Natural Resources

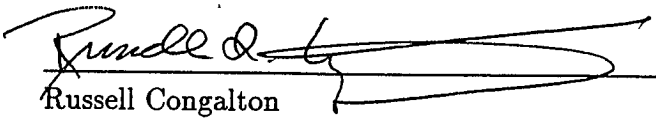
September 1994

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

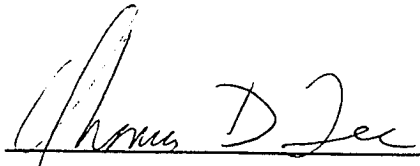
This dissertation has been examined and approved.



Dissertation director, John D. Aber
Professor of Forest Resources

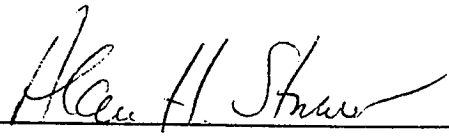


Russell Congalton
Associate Professor of Remote Sensing and GIS



Thomas D. Lee
Associate Professor of Plant Biology

Barrett Rock
Associate Professor of Forest Resources



Alan Strahler
Professor of Geography, Boston University

August 1, 1994
Date

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

ACKNOWLEDGMENTS

I would like to thank my committee members for their support and advice during the course of this project: John Aber, Russell Congalton, Tom Lee, Barrett Rock and Alan Strahler. My special thanks to John Aber for providing the inspiration, encouragement and guidance that have made this work possible.

The collection and analysis of field data would not have been possible without the hard work of Jennifer Ellis, Steve Newman, Rich Hallett, Margaret Soulia, Alison Magill, Gloria Quigley, Brian Kloeppel, Suzanna Walter, and Jim Muckenhoupt.

I would also like to thank those involved in NASA's Accelerated Canopy Chemistry Program who have provided support in the collection and analysis of AVIRIS data: Robert Green, Howell Johnson, Kathy Heidebrecht, Roger Clark, Gregg Swayze, Carol Wessman, Joe Boardman, Mark Helmlinger, Jeanette van den Bosch and many others.

During the past ten years I have been very fortunate to share my life and studies with Jon Chappell. Jon has contributed many hours directly to this project, but most of all his love, encouragement, and sense of humor have helped me complete this work.

This research was funded in part by the Harvard Forest Long Term Ecological Research Grant (NSF #BSR-8811764), EOS: High Resolution Imaging Spectrometer Science Team (NASA contract #NAS5-31379), and the HIRIS Accelerated Canopy Chemistry Program (NASA grant #NAGW3194).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

TABLE OF CONTENTS

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

LIST OF TABLES

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

LIST OF FIGURES

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

ABSTRACT

MEASUREMENTS OF FOLIAR CHEMISTRY USING LABORATORY AND AIRBORNE HIGH SPECTRAL RESOLUTION VISIBLE AND INFRARED DATA

by

Mary E. Martin
University of New Hampshire, September, 1994

Remote sensing of foliar chemistry has been recognized as an important element in producing large scale, spatially explicit estimates of forest ecosystem function. Visible and near infrared reflectance measurements of forest foliage, at both the leaf and canopy scales, were studied in an effort to relate spectral data to foliar chemical composition. At the scale of the individual leaf, near infrared spectra and chemical data were collected from 211 fresh leaf samples, including 17 different hardwood and conifer species. Reflectance data at selected near infrared bands was closely related to the nitrogen, lignin, and cellulose concentration of these leaf samples, with correlation coefficients greater than 0.83. In order to make large-scale regional estimates of foliar chemistry, this study was extended to whole forest canopies. Foliage and leaf litter were sampled on forty plots at Blackhawk Island, Wisconsin and Harvard Forest, Massachusetts to determine canopy level nitrogen and lignin concentrations. At the time of the field sampling, spectral measurements of the canopy were made with NASA's Airborne Visible/Infrared Imaging Spectrometer,

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

a high spectral resolution instrument. Calibration equations were developed from these field and spectral data (R^2=.87 and .77 for nitrogen and lignin, respectively). These equations were applied to all image pixels to make spatially explicit estimates of canopy nitrogen and lignin for both study sites. These estimates of nitrogen and lignin concentrations were then used with existing ecosystem models to predict carbon balance at Harvard Forest and nitrogen mineralization rates at Blackhawk Island. The chemical analysis of leaf samples collected from the study sites revealed that foliar nitrogen and lignin concentrations could be used to identify samples by species. The spectral bands used to measure nitrogen and lignin were then used to identify 11 different species classes at the Harvard Forest. A comparison of field measured species composition to the classification showed an overall accuracy of 73.4%. These results indicate that airborne and spaceborne imaging spectrometers will provide important information for the study of forest ecosystems.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Chapter 1

INTRODUCTION

Large scale assessments of nutrient cycling and carbon balance in forested ecosystems are critical in understanding the role of forests in global nutrient and energy cycles. Documentation and monitoring of global change, occurring in response to climatic change and human activity, requires that forest ecosystem processes be measured on a large scale. The chemical composition of the forest canopy can be used as an indicator of critical ecosystem processes. For example, litter decomposition, nutrient cycling, photosynthetic rates and carbon storage have all been closely related to foliar chemical composition in previous studies (Aber and Melillo 1982; Melillo *et al.* 1982; McClaugherty *et al.* 1985; Field and Mooney 1986; McClaugherty and Berg 1987; Wessman *et al.* 1988b; Reich *et al.* 1992).

Traditionally, measurements of ecosystem processes have been made by small-scale plot level studies and extrapolated to larger areas. Remote sensing data acquired by satellite and aircraft sensors now offer the potential to view the earth repeatedly, and over large areas. Studying forest ecosystems in this manner adds a spatial dimension to ecosystem studies unavailable with traditional plot level sampling. In the mid 1980's remote sensing technology advanced with the development of airborne instruments having high spectral resolution imaging capabilities (Goetz *et al.* 1985; Vane and Goetz 1988). Data from two high spectral resolution instru-

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

ments, the Airborne Imaging Spectrometer (AIS) and the Airborne Visible/Infrared Imaging Spectrometer (AVIRIS), have been used in a number of studies to measure canopy biochemistry (Peterson *et al.* 1988; Wessman *et al.* 1988b, 1989; Johnson *et al.* 1994; Matson *et al.* 1994).

The primary goal of this research is to estimate forest ecosystem processes over a large area using the measurement of physical canopy characteristics via airborne remote sensing instrumentation. We have investigated the relationships between remotely sensed high spectral resolution AVIRIS data and foliar chemistry, and we apply our estimates of canopy chemistry to existing models of ecosystem processes dependent on forest canopy chemistry (i.e. carbon balance and nutrient cycling) (Wessman *et al.* 1988b; Aber and Federer 1992).

There are a number of fundamental questions which must be addressed if we are to be successful in meeting our objectives:

1. What are the relationships between the chemical composition of fresh foliage and high resolution *laboratory* spectra?

2. What are the relationships between the chemical composition of the forest canopy and and high resolution *remotely sensed* spectra, and can we use these relationships to drive ecosystem models of carbon balance and nutrient cycling?

3. If the chemical content can be successfully determined using remotely sensed high spectral resolution data, can we use this information to determine the species composition of the canopy?

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

The format of this thesis is structured such that the introduction and literature review chapters are followed by three independent papers addressing the questions enumerated above.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Chapter 2

BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

Since the primary absorption features in plant materials occur in the infrared region of the spectrum, we begin our review with a discussion of the principles of near infrared (NIR) absorbance. This is followed by a discussion of NIR absorbance in plant materials and its relationship to leaf chemical composition. This chapter concludes with a discussion of the relationships between foliar chemistry and ecosystem processes.

2.2 Principles of NIR Spectroscopy

The interaction of electromagnetic radiation with molecular bonds is the fundamental building block of near infrared (NIR) spectroscopy. For this particular wavelength region and application, a wave model can be used to describe the behavior of electromagnetic (EM) radiation. In a wave model, EM radiation is described by continuously alternating electric and magnetic field intensities that are perpendicular to the direction of travel (Halliday and Resnick 1986). An EM wave can be characterized by its frequency (i.e., the rate at which the electric field alternates) and by the intensity (or amplitude) of the field (Murray and Williams 1987).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

In its simplest form, one can consider the molecular bonds that are effected in this wavelength domain as primarily dipole in nature - such as H_2O. In a dipole molecule there is an asymmetric charge distribution due to the bonding of the constituent atoms. These molecules are free to respond to a repetitive forcing function - such as an alternating electric field - if the forcing frequency of the field is near the resonant frequency of the molecule. The molecule can respond with a number of vibrational modes, such as a rotation about the center of mass and/or a compression/stretching along the dipole axis (Murray and Williams 1987). The rotational frequencies are determined by the length of the dipole and the mass of the molecule. The characteristic compressional absorption frequencies are determined by the bonding forces along the dipole axis and the molecular mass. In more complex molecules, such as aromatic ring structures, additional vibrational modes can be induced (i.e., bending).

Frequencies which excite these vibrational modes are absorbed by the molecule, and the energy of the EM radiation is transformed into thermal energy (i.e., the motion of the molecule). Since each molecular structure has a unique charge and mass distribution this will result in a characteristic absorption spectrum for each molecule. This characteristic absorption spectrum is a result of the three primary vibrational modes - rotation, compression and bending.

Fundamental molecular absorption occurs in the mid infrared (MIR) region (2.5-15μm). Absorption also occurs at integer multiples of the primary absorption bands. These are referred to as overtone (or harmonic) absorption bands, with the first overtone being the strongest. Combination bands are also absorbed by the sample - these

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

bands occur when the energy of the electromagnetic radiation is equal to the sum of two or more molecular bond resonant frequencies (Murray and Williams 1987). Barton II *et al.* (1992) measured agricultural samples with both NIR and MIR instruments and calculated the two dimensional correlation between absorbance in the NIR and MIR spectra. High correlations were found between fundamental MIR absorptions for C-H, C=O, C=C, and N-H and the corresponding absorption overtones in the NIR region.

2.3 NIR Absorption in Leaves

Many different molecular bonds are found in the constituents of leaves. In this work we are primarily interested in the absorption of EM radiation by lignin and nitrogen molecules. The bonds in these molecules to which characteristic NIR absorption is most commonly attributed are C-H, O-H, and N-H, as overtones of the fundamental MIR absorption frequencies. Several reviews have been made of the molecular absorption characteristics of these molecules. A thorough qualitative review of absorption features in plant constituents can be found in Williams and Norris (1987) and Osborne and Fearn (1986). These works present tables of absorption bands as well as NIR spectra (.8-2.5μm) for amino acids, protein, cellulose, sugar, and lignin. Weyer (1985) also reviews specific absorption features of C-H, O-H, and N-H bonds in organic substances.

Protein molecules, consisting of amino acids, contain many N-H bonds. The primary absorption features in the NIR attributed to proteins are 1510, 1980, 2050,

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

2180, and 2240nm (Osborne and Fearn 1986). These are due primarily to the stretching and bending of N-H bonds.

Lignin is a phenolic compound containing aromatic functional groups. An analysis of dioxane lignin by Barton II *et al.* (1992) shows strong absorption features at 1314nm (C-H overtone), 1666 and 1792nm (aromatic overtone), and 1442 and 1672nm (C=C aromatic stretch). Other studies have identified 1256, 2090, 2260 and 2330nm as absorption features attributable to lignin molecules (Elvidge 1988; Wessman *et al.* 1988a).

Although pure leaf compounds may show distinct absorption peaks, these features are less obvious in the spectra of whole leaves. Certain bonds, such as O-H are found in protein, lignin, and cellulose molecules making it difficult to use a single absorption feature to determine one compound.

2.4 Quantitative NIR Analysis

The discussion so far has covered the *qualitative* aspects of NIR absorption features in organic molecules. Within the last 20 years NIR spectroscopy has become a widely used method for the *quantitative* analysis of constituent molecules in agricultural products.

The use of NIR spectroscopy to make such measurements is based on the relationship expressed by the Beer-Lambert Law. This relationship is described by the following equation:

$$log(\frac{1}{R}) = klc$$

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

where k is the molecular absorption coefficient of the constituent, l is the pathlength through the sample, and c is the concentration of the constituent in the sample (Dixit and Ram 1985; Murray and Williams 1987). This relationship states that the absorption of NIR radiation by a molecule is proportional to the molecular absorption coefficient, the pathlength, and the concentration of the molecule in the sample. In NIR spectroscopy, the pathlength of the sample is kept constant by using a sample cell of a set depth, leaving absorption to vary linearly with concentration.

NIR instruments are calibrated by making absorption measurements on a sample set for which the traditional laboratory analysis (reference method) has been made. The NIR measurements of the calibration samples are then related by multiple linear regression equations to the values obtained by the reference method. The NIR absorbance data $[\log(\frac{1}{R})]$ is commonly transformed, by one of several mathematical treatments, into a variable used in the regression equation. Most often, a first or second difference transformation is used in developing calibration equations. This transformation serves two functions: 1) to remove the effects of baseline shifts and 2) to discriminate between overlapping bands (Dixit and Ram 1985; Hrushcka 1987). Baseline shifts between samples are often a result of increased absorption uniformly across the spectra due to differences in scattering, which can be attributed to differences in particle size. Higher order difference transformations will also remove baseline shift and separate overlapping bands but at the same time generate artifacts from the noise in the spectra (Hrushcka 1987). The first difference (λ_i') and second difference (λ_i'') are calculated as:

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

$$\lambda_i' = < \lambda_{i+.5d} > - < \lambda_{i-.5d} >$$

$$\lambda_i'' = < \lambda_{i+d} > - 2 < \lambda_i > + < \lambda_{i+d} >$$

where $< \lambda_i >$ is the mean absorbance value centered at λ_i for a specified spectral bandwidth, and d is the distance between band centers.

The multiple linear regression equations generated during the calibration process have the form:

$$\% \text{ constituent} = b_o + \sum_{i=1}^{n} b_i x_i$$

where x_i is the absorbance value (or difference) at selected wavelengths and b_i is the fitting coefficient for each wavelength. A minimum number of terms are used to avoid overfitting the equation to the calibration data. Several tests described by Hrushcka (1987) are available to determine if overfitting has occurred.

More recently, the method of partial least squares (PLS) has been used in developing NIR calibration equations (Lindberg *et al.* 1983; Sjostrom *et al.* 1983; Lindberg *et al.* 1985). This method generates PLS factors which describe the variation of the NIR spectra as it relates to the calibration data. A major difference between this method and the multiple linear regression technique is that PLS uses information from *all* wavelengths to predict concentration. As in multiple linear regression techniques, it is possible to under- and over-fit the data.

The calibration techniques for NIR spectroscopy are empirically based, although

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

there is an understanding of the fundamental principles causing absorption. In part, this is due to the complexities of the organic compounds as they exist in foliage. It is possible to measure the spectra of pure leaf constituents. However, these components may absorb NIR radiation differently when they are combined with other leaf constituents.

2.5 NIR Measurements of Foliar Constituents

2.5.1 Dried Plant Materials

The NIR analysis of vegetation began first in the agricultural community. Calibration equations were developed for crude protein, lignin, starch, sugar and oils in forage crops (Norris *et al.* 1976; Shenk *et al.* 1979; Williams *et al.* 1985). This method of analysis became widely used within a short period of time and has recently become a standard analytical technique in the agricultural field (Barton II and Windham 1988).

In 1988 this method was first used for the chemical analysis of forest foliage samples (Wessman *et al.* 1988a). The 203 samples in this study included 20 tree species (both hardwood and conifer) as well as several grass species. These samples were both dried green leaves and dried undecomposed litter. Nitrogen concentration was related to first difference spectra, where a linear equation using five wavelengths was produced (R^2=0.98, Standard error of calibration (SEC)=0.11). Four of the wavelengths used were known to be protein absorption features. Lignin concentration was best predicted with the second difference absorbance spectra. A six term

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

equation was developed with an R^2 of 0.78 and SEC of 2.90.

Further work was done with dried ground foliage samples by Card *et al.* (1988). In this study, foliage samples were used from a wide geographic range and included green leaf and litter samples from coniferous and deciduous species. The NIR analysis technique was used to predict starch, protein, sugar, cellulose, chlorophyll, lignin, and nitrogen. The results of NIR analysis differed widely, with some constituents highly correlated with NIR absorbance (nitrogen, chlorophyll, and protein) and others (i.e., cellulose) showing little relationship.

These studies were the first of this type to use this method for *forest* foliage analysis. Since that time, this method has been used in an operational mode for the analysis of nitrogen, lignin and cellulose in forest foliage (McLellan *et al.* 1991a). The current equations in use cover a wider range of tree species and predict nitrogen, lignin and cellulose concentrations for dried and ground green leaves and litter.

There are a number of advantages to using NIR spectroscopy for foliar chemistry analysis in place of traditional wet chemistry techniques. First, the analysis can be made quickly. The sample is prepared in the same manner as for wet chemistry (ground and dried), but the actual analysis takes approximately 5 minutes per sample compared to traditional analysis which can take up to a week for the analysis of twenty samples. Analysis of fresh leaf samples does not require any sample preparation. Additionally, NIR spectroscopy does not require the use of any chemicals beyond those which are used in the analysis of calibration samples. This method not only makes for a safer analysis but also saves cost in the purchase and disposal of chemicals.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Unlike wet chemistry analyses, the NIR technique uses one spectral measurement to measure all of the constituents for which a calibration equation exists. In addition, the technique is nondestructive, allowing for further analysis by a different method. The repeatability (precision) of measurements made by this technique is better than that which can be obtained with wet chemical analysis (Barton II 1987; McLellan *et al.* 1991a).

The cost per sample is lower for NIR analysis as compared to wet chemistry. The initial startup cost can be high for the instrument and analysis of the calibration samples, but future labor and supply costs are lower than that for wet chemistry methods. The practice of intercalibrating instruments and using established calibration equations is reducing some of this cost.

The disadvantages of NIR analysis are the instrumentation cost, dependence on calibration procedures, complexity of possible data treatments, and lack of sensitivity for minor constituents (Marten *et al.* 1989).

2.5.2 Fresh Plant Materials

The success of NIR analysis for dried, ground leaf samples has further evolved to the analysis of fresh leaf materials. The fresh NIR leaf spectra is dominated by the absorption of water. Water absorption occurs throughout the NIR spectra, with distinct absorption features centered at 1.4 and 1.9μm. In order to use remote sensing data to measure canopy chemistry, the signal due to chemical composition must not be masked by these water absorption features. Several studies have investigated the analysis of foliar chemistry using NIR spectrometry at both the leaf and canopy

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

level using laboratory and remote sensing data, respectively.

Laboratory Studies

Laboratory spectral analysis of fresh green leaves represents a logical step between the analysis of dried leaf materials and remote sensing of whole canopies. Peterson *et al.* (1988) measured the reflectance of fresh conifer needles. Using a first difference spectral transformation, both nitrogen and lignin were correlated with spectral measurements (although not as strongly as in dried, ground samples). A larger fresh leaf sample set collected and analyzed by Martin and Aber (1990), consisted of 60 samples, including twelve species of conifer and deciduous leaves. The chemistry of these leaf samples was correlated with selected second difference NIR bands. Nitrogen, lignin, and cellulose were related to spectral measurements with regression equations using three wavelengths. The R^2 of these analyses were .89, .88 and .82, respectively, standard errors of calibration were 0.18% nitrogen, 1.91% lignin, and 3.54% cellulose.

Remote Sensing Studies

Remote sensing of canopy biochemistry has become recognized as an important tool in detecting ecosystem response to increasing atmospheric CO_2 and increasing nitrogen deposition (Wessman 1990).

The results of laboratory NIR measurements of fresh foliar chemistry suggests that spectral signatures related to leaf constituent concentration may be present at the canopy level.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Two instruments have been designed and built by NASA's Jet Propulsion Laboratory which cover the spectral range desired for canopy chemistry research. The Airborne Imaging Spectrometer (AIS), in use during the 1980's, was used for canopy chemistry research (Goetz *et al.* 1985; Vane and Goetz 1988). At the present time, the Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) is being flown over a number of sites at which canopy chemistry research is taking place.

Wessman *et al.* (1988b, 1989) and Peterson *et al.* (1988) used AIS data to measure canopy chemistry at Blackhawk Island and the University of Wisconsin Arboretum. These studies were based on field data collected on a total of 18 plots. Spectral data were available only for the spectral range of 1.2-1.6μm due to instrument problems. In this spectral range, bands of the first difference spectra were correlated with canopy lignin and nitrogen. The primary absorption band used in the lignin analysis, 1256nm, was attributed to C-H vibrations in lignin molecules. Bands centered at 1555 and 1265 were used to predict canopy nitrogen concentration. This analysis was done with both conifer and hardwood species.

Remote sensing of canopy chemistry has also taken place in the the Oregon Transect Ecosystem Research Project (OTTER), a study of biogeochemical cycling along a climatic and fertility gradient (Peterson and Waring 1993). Canopy nitrogen, lignin and starch concentration (and content), measured by field collection, were correlated with first difference AVIRIS spectra (Johnson *et al.* 1994; Matson *et al.* 1994).

Two important goals in the remote sensing of foliar chemistry will be to develop generalizable algorithms which can be used to convert radiance data to foliar

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

chemistry estimates, and to identify and implement models which convert spatial estimates of foliar chemistry into estimates of ecosystem processes.

Until recently, few studies have used data in the full spectral range (visible and infrared) or have covered a wide geographic and species range. It has been the goal of NASA's Accelerated Canopy Chemistry Program (ACCP) to provide high quality (high signal:noise) high spectral resolution remote sensing data from AVIRIS to a number of researchers studying diverse forest ecosystems.

2.6 Ecosystem Processes Related to Foliar Chemistry

The primary value in the remote sensing of foliar chemistry is the relationship between foliar chemistry and critical ecosystem processes. Foliar lignin is closely related to nitrogen mineralization rate by its influence on litter decomposition. Foliar nitrogen concentration is related to the rate of photosynthesis and therefore ecosystem carbon storage.

2.6.1 Foliar Lignin

The decomposition of leaf litter can be divided into three basic stages (Berg *et al.* 1984; Aber and Melillo 1991). The first stage is the loss of soluble substances such as sugars beginning at litterfall. The second stage is the loss of insoluble polymer carbohydrates such as cellulose. This stage of decomposition also begins shortly after litterfall. The substances broken down in this phase of decomposition yield sufficient amounts of energy to allow population growth of microbial decomposers, and is often accompanied by immobilization of nitrogen or other limiting nutrients. The third

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

stage of decomposition begins when soluble compounds have been depleted - and remaining cellulose is shielded by lignin and is not directly accessible to microbial attack. At this point in decomposition the remaining materials are 1) lignin, 2) humus-like phenolic compounds which were formed as decomposition by-products in earlier stages, and 3) cellulose remaining in close physical association with lignin. Cellulose and lignin do not decompose independently; lignin must be removed to expose the remaining cellulose to microbial attack.

The molecular structure of lignin causes it to be very resistant to decomposition. The complex 3-D structure of lignin molecules shield the lignin itself as well as the closely associated cellulose from microbial attack. Such a large amount of energy is required to break down this complex molecular structure that there is no net yield of energy from this process. In the third stage of decay, the decomposition of lignin is the rate limiting factor in any further decomposition.

The process of decomposition converts nutrients in organic compounds into the inorganic forms used by vegetation (i.e., NO_3, NH_4). The nutrients released in litter decay are used by microbes and vegetation. In the early stages of decomposition, the growing microbial population cannot be supported by the nutrients in the litter. For a period of time, nutrients are incorporated into the litter from the soil solution. During this nutrient immobilization period, the absolute amount of certain nutrients increases (i.e., nitrogen, phosphorous, and sulphur). During later stages of decay the demand for nutrients declines and a period of mineralization occurs in which nutrients are made available for use by the vegetation.

The rate at which leaf litter decomposes is a function of both litter composition

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

and climatic factors. The climatic variables affecting litter quality have been studied by Meentemeyer (1978) and Upadhyay *et al.* (1989). In these studies actual evapotranspiration (AET) was used as a climatic index, and for certain climates (cooler) was found to be a better predictor of decay rate than litter quality, indicating that the degree to which lignin influences the decomposition rate of litter may vary with climate.

Many studies have linked the rate of decomposition to litter quality. Litter quality is quantified by several different criteria. The discussion of litter decomposition studies which follows will include those which quantified litter quality as %lignin, %nitrogen, cellulose:lignin ratio, lignin:nitrogen ratio, and the holocellulose:lignocellulose ratio.

Fogel and Cromack (1976) studied decomposition in douglas fir foliage, and found that litter decayed in a manner consistent with the patterns described by Olson (1963); %mass remaining = e^{-kt}, where k is the litter decay constant, and t is time. In this study the litter decay constant was more closely related to the lignin concentration than the C:N ratio in the douglas fir foliage.

Melillo *et al.* (1982) examined the effects of nitrogen and lignin on leaf litter decay in six temperate (New Hampshire) hardwood species. A strong relationship was found between initial lignin:nitrogen ratio and decomposition rate in these species. This relationship was also strong in the data previously collected by Fogel and Cromack (1976) which included both conifer and hardwood species in North Carolina. Although this relationship exists at both sites, the North Carolina litter decomposed more rapidly for a given L:N ratio than the litter decomposed in New Hampshire

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

due to the climatic differences. This same study also confirms that the exponential decay process holds true for the decomposition data of Daubenmire and Prusso (1963), a study which included both hardwood and conifer species.

McClaugherty and Berg (1987) studied litter decomposition in several conifer and deciduous species in Sweden. Litter quality was assessed with the holocellulose:lignocellulose quotient(HQL), with holocellulose including cellulose and hemicellulose. These litter samples were in the late stages of decomposition. At this stage the HLQ is low (most of the lignocellulose fraction is lignin) and the nitrogen fraction is high. This study found that the HQL was highly correlated with annual litter mass loss as was nitrogen concentration.

White *et al.* (1988) compared litter decomposition in a black locust and pine-hardwood stand in North Carolina. This study found that lignin alone, and the cellulose:lignin ratio were significantly correlated with litter mass loss. Lignin:nitrogen ratio was also significant if black locust was excluded from the analysis. This species did not fit the usual pattern because the high foliar nitrogen concentration causes a low L:N ratio in litter having a relatively high lignin concentration and slow decomposition rate.

A study by Upadhyay *et al.* (1989) found that lignin concentration was the most important litter quality variable related to the rate of decomposition for ten species of Central Himalayan leaf litter. Their best model for predicting litter mass loss included either AET or mean annual temperature as well as lignin concentration.

Schaefer *et al.* (1985) found no relationship between litter chemistry and decomposition rate in shrubs and herbaceous plants in a North American desert. This

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

paper also shows that AET does not effect decomposition in surface litter but does in buried litter. Although this litter was mostly herbaceous it is important to note that under certain climatic conditions lignin does not control decomposition.

The studies mentioned above clearly demonstrate that the chemical composition of leaf litter is a major determining variable in the rate of decomposition. For most species and climatic conditions, lignin concentration, or some combination of lignin and other litter constituents, can be used to predict the rate of litter decay. This inverse relationship between lignin concentration and decomposition rate holds true for both conifer and hardwood species (Melillo *et al.* 1982).

2.6.2 Foliar Nitrogen

A number of studies have investigated the relationships between foliar nitrogen concentration and photosynthetic capacity. Field and Mooney (1986) summarized data from 12 studies in which both photosynthetic capacity and total organic nitrogen were measured on a leaf weight basis. In both greenhouse and naturally grown herbaceous and tree species, they found positive correlations between photosynthetic capacity and nitrogen concentration.

A number of hardwood species, studied by Reich *et al.* (1991), showed a positive relationship between measurements of both mass and area based nitrogen and photosynthetic capacity. These relationships were seen *within* each species as foliar nitrogen varied seasonally.

In Aber and Federer (1992), data composited from previous studies on the photosynthetic rates and nitrogen concentration of broad-leaved northeastern forest

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

species, yield a similar relationship by which ecosystem carbon balance is modeled.

Developing the capability to remotely measure canopy chemistry will provide a neccessary tool for the assessment of carbon and nutrient cycling in forest ecosystems on a regional scale. The ability to make spatially explicit measurements of these processes will greatly increase the amount of information available on the role of forests in regional and global biogeochemical cycles.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Chapter 3

DETERMINING THE CHEMICAL COMPOSITION OF FRESH LEAVES USING NEAR INFRARED SPECTRA

3.1 Introduction

The chemical composition of canopy foliage is related to ecosystem processes such as plant productivity, litter decomposition rates, and nutrient availability (Melillo *et al.* 1982; Wessman *et al.* 1988b). Long term, large scale monitoring of these processes is crucial to understanding the dynamics of global change. Such monitoring programs will require that relationships between remotely sensed spectral data and these processes be derived. A significant amount of work has been done to correlate near infrared (NIR) spectra with the chemical composition of *dried*, ground plant material (Williams and Norris 1987). In this paper we have extended this work to investigate the correlations between NIR spectra and the chemical composition of *fresh* forest foliage. Establishing this link between the NIR spectra of fresh, whole leaves and their chemical composition is essential in making foliar chemistry measurements from airborne or spaceborne remote sensing platforms.

There is a long history of NIR spectroscopy in agriculture disciplines for the measurement of chemical constituents in plant materials. This method involves correlating selected NIR wavelengths with chemical constituent concentrations measured

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

by wet chemistry methods (Norris *et al.* 1976; Shenk *et al.* 1979). Constituents such as crude protein, total nitrogen, fiber, lignin, cellulose, and moisture have been successfully measured by this method (Norris *et al.* 1976; Shenk *et al.* 1979, 1981; Williams *et al.* 1984, 1985; Abrams *et al.* 1988). This technique has more recently been applied to the analysis of constituents in the foliage of native woody plants (Card *et al.* 1988; Wessman *et al.* 1988a; McLellan *et al.* 1991a). In these studies, correlations were made between the laboratory NIR spectra of dried, ground samples and the nitrogen, lignin and cellulose concentrations as measured by wet chemistry methods.

At the canopy level, reflectance measurements made over a narrow region of the NIR spectra (1200-1600nm) from NASA's Airborne Imaging Spectrometer (AIS) were used to estimate canopy nitrogen and lignin in 18 Wisconsin forest sites (Peterson *et al.* 1988; Wessman *et al.* 1988b, 1989). In this work, correlations were made between remotely sensed NIR spectra of the forest canopy (including spectral information from an ensemble of leaves) and the canopy chemistry as derived from ground measurements. As part of the HIRIS team under NASA's Earth Observing System (EOS) program, we are investigating the correlation between leaf chemistry and NIR spectra at three levels; 1. dry, ground leaves, 2. fresh leaves, and 3. whole canopies. In this paper we discuss our investigation into the leaf level relationships between near infrared reflectance of *fresh* forest foliage and concentrations of nitrogen, lignin, and cellulose.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

3.2 Methods

Two hundred eleven foliage samples from 6 needle-leaved and 11 broad-leaved tree species were collected at several locations within New Hampshire and Massachusetts. Samples were placed in plastic bags and refrigerated between time of collection and spectral measurement. NIR spectral measurements were made within 24 hours of collection. All spectra were measured by an *NIRSystems Model 6250* Near Infrared Spectrophotometer. In order to prevent light from reflecting off the back of the sample holder, each broad-leaved sample consisted of a stack of 9-10 leaves. When 6 or more leaves were used, there was no detectable difference in the NIR spectra. All samples were scanned four times, with the sample cell rotated 90° between scans, and with the leaves restacked between the second and third scans. Conifer needles were removed from the branches, packed firmly into the sample cell, and scanned four times. The sample cell was scanned, rotated 90° and scanned again, the sample was then stirred and the scans repeated. For analysis we used the average of the four scans of each sample. The spectral measurements ranged from $1100 - 2500nm$ and were reported as absorbance ($\log(R^{-1})$) with respect to a ceramic reference standard. Data are reported at $2nm$ intervals with an instrument bandwidth of approximately $10nm$.

Samples were then prepared for NIR chemical analysis using the dried, ground sample technique. The concentrations of nitrogen, lignin, and cellulose in these samples were determined by NIR analysis as described by McLellan *et al.* (1991a). This method uses linear regression equations derived from a calibration data set

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Species	n	Nitrogen		Lignin		Cellulose	
		$\bar{x}$	σ	$\bar{x}$	σ	$\bar{x}$	σ
Beech	20	1.78	0.23	19.66	1.03	45.43	2.64
Red Oak	12	1.66	0.14	19.64	3.30	40.07	2.30
Sugar Maple	18	1.46	0.28	11.25	1.31	34.79	2.06
White Birch	4	2.07	0.04	11.10	0.32	36.20	0.33
Balsam Fir	14	1.14	0.12	24.35	0.84	27.83	2.95
Norway Spruce	20	1.11	0.07	18.04	1.55	35.84	2.56
Red Spruce	14	1.09	0.07	21.84	1.32	34.58	1.22
Poplar	3	2.05	0.13	17.70	2.34	30.27	4.42
Hickory	15	1.94	0.14	13.67	2.22	47.16	2.00
Gray Birch	18	1.85	0.22	18.59	2.64	35.31	2.64
Red Maple	12	1.55	0.14	17.56	5.04	32.07	7.01
White Pine	6	1.18	0.05	24.78	1.01	32.63	2.03
Red Pine	6	1.17	0.08	22.55	2.27	37.12	1.52
White Ash	10	1.83	0.27	16.34	1.50	42.81	2.28
Hemlock	16	1.21	0.07	17.19	1.67	41.89	1.37
Black Cherry	3	2.01	0.04	11.42	0.38	40.96	0.81
Black Birch	20	1.84	0.35	15.51	1.82	39.03	3.48
Total	211						

Table 3.1: Description of samples used in this study. $\bar{x}$ = mean percent constituent by weight as determined by NIR analysis of dried, ground material, σ = standard deviation.

in which both dried, ground leaf spectra and wet chemistry measurements were available for each sample. Table 3.1 describes the chemical composition of the sample set as derived by this method.

3.3 Analysis

For all comparisons presented, "measured" refers to constituent concentrations as determined by NIR analysis on dried, ground samples (McLellan *et al.* 1991a). The fresh foliage spectra were compared with measured values in three ways: First, the same equations used for dry ground samples (Table 3.2) were applied to the fresh sample spectra to predict concentrations. Second, a new set of predictive equa-

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

tions was derived using the same wavelengths as for dried ground samples but with new fitting coefficients calculated. Third, new wavelengths and coefficients were derived for each constituent. For the first comparison, all samples represented a validation set and were not separated. For the second and third, samples were randomly assigned to either a calibration (n=147) or validation (n=64) set. Calibration samples were used in the regression calculations with validation samples remaining separate to evaluate predictions. A second difference transformation of the NIR absorbance spectra was used in developing the calibration equations. This transformation serves two functions: 1) to remove the effects of baseline shifts and 2) to discriminate between overlapping bands (Martin 1966; Dixit and Ram 1985; Hrushcka 1987). Baseline shifts between samples are often a result of increased absorption uniformly across the spectra due to differences in scattering and/or noise. The second difference (λ_i'') is calculated as:

$$\lambda_i'' = < \lambda_{i+d} > - 2 < \lambda_i > + < \lambda_{i-d} >$$

where $< \lambda_i >$ is the mean absorbance value centered at λ_i for a spectral bandwidth of 20nm, and d is the distance between band centers.

Multiple linear regression analysis (Casciero and DiGiovanni 1985) was then used to relate second difference spectra to nitrogen, lignin, and cellulose concentrations (by weight). The equations derived from these methods are of the form:

$$\text{Concentration}(\%) = b_o + \sum_{i=1}^{n} b_i \lambda_i''$$

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

where λ_i'' is the second difference absorbance value at selected wavelengths, and b_o and b_i are the linear fitting coefficients.

In order to test the calibration equations for overfitting we used the three tests described in Hrushcka (1987). The three to four wavelengths selected for each equation were based on correlations with the constituent of interest. These selected wavelengths are correlated with absorption bands associated with molecular bonds found in the samples.

3.4 Results and Discussion

For the first comparison, predicting fresh leaf chemistry with dry leaf equations, the goodness of fit for nitrogen is relatively high compared to that of lignin and cellulose (Table 3.2). This high nitrogen correlation occurs because the first nitrogen wavelength alone, 2170nm, is highly correlated with nitrogen concentration and is not located near the water absorption features of the spectrum. The major water absorption bands in fresh leaf foliage are centered at 1450 and 1940nm. In contrast, terms used to predict lignin and cellulose in dried ground samples fall within the water absorption features and predictions for fresh foliage do not correlate well with measured values (Table 3.2).

Using the *same wavelengths* which are used in the dry leaf equations (comparison 2), we derived new coefficients to fit the fresh spectra to chemical composition. Predictions made with the second approach (same wavelengths, different coefficients) have higher correlation coefficients than the previous analysis for all

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Constituent	Coefficient		Wavelength		SEC	Rc	SEP	Rp	SEPC	Rp
					dry leaves		dry leaves		fresh leaves	
Nitrogen	b_o	1.33			0.12	0.98	0.15	0.98	0.20	0.85
	b_1	-138.18	λ_1	2170						
	b_2	-28.87	λ_2	1686						
	b_3	-22.07	λ_3	1978						
Lignin	b_o	-0.52			2.53	0.88	2.86	0.60	14.00	0.49
	b_1	-40.05	λ_1	1438						
	b_2	-1151.30	λ_2	2386						
	b_3	-807.06	λ_3	2218						
	b_4	1459.38	λ_4	1828						
Cellulose	b_o	47.20			2.63	0.90	3.23	0.76	14.00	0.41
	b_1	1170.00	λ_1	2140						
	b_2	2890.37	λ_2	1766						
	b_3	-909.39	λ_3	1960						
	b_4	1023.22	λ_4	1982						

Table 3.2: Calibration equations developed for dried, ground leaf samples and applied to both dry and fresh leaf spectra. Calibration results for fresh leaf samples, SEC = standard error of calibration, Rc = correlation coefficient of calibration, SEP = standard error of prediction, Rp = correlation coefficient of prediction, SEPC = bias corrected error of prediction

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Constituent	Coefficient		Wavelength		SEC	Rc	SEP	Rp
Nitrogen	b_o	2.59			0.18	0.88	0.15	0.90
	b_1	-132.75	λ_1	2170				
	b_2	-65.71	λ_2	1686				
	b_3	-25.70	λ_3	1978				
Lignin	b_o	11.03			2.27	0.85	2.39	0.83
	b_1	332.41	λ_1	1438				
	b_2	-149.38	λ_2	2386				
	b_3	1069.40	λ_3	2218				
	b_4	20.13	λ_4	1828				
Cellulose	b_o	63.98			3.88	0.74	4.27	0.72
	b_1	1106.81	λ_1	2140				
	b_2	1099.03	λ_2	1766				
	b_3	390.42	λ_3	1960				
	b_4	-201.96	λ_4	1982				

Table 3.3: Calibration results for fresh leaf samples, using the same wavelengths as the dry calibration, SEC = standard error of calibration, Rc = correlation coefficient of calibration, SEP = standard error of prediction, Rp = correlation coefficient of prediction

three constituents for samples in both calibration and validation sets (Table 3.3). This suggests that absorbance features at these wavelengths are modified by water absorption, but not to such a degree that the information on chemical composition is completely obscured.

In the third approach, new wavelengths were chosen due to their statistical fit to the data and their relationship to known absorption features of molecular bonds present in the samples. All nitrogen wavelengths were selected on the basis of correlation. For lignin and cellulose, the first wavelength was chosen based on known absorption features with the remainder chosen on a statistical basis. A better statistical fit can be obtained strictly by correlation. However, equations based strictly on correlation may not be generalizable to other samples. The equations derived from this method have higher multiple correlation coefficients than the equations

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Constituent	Coefficient		Wavelength		SEC	Rc	SEP	Rp
Nitrogen	b_o	1.84			0.12	0.95	0.13	0.94
	b_1	-111.36	λ_1	2174				
	b_2	55.02	λ_2	2128				
	b_3	24.14	λ_3	1712				
Lignin	b_o	10.01			1.78	0.91	1.69	0.92
	b_1	-969.50	λ_1	2260				
	b_2	685.62	λ_2	2330				
	b_3	525.24	λ_3	2078				
	b_4	-271.61	λ_4	1648				
Cellulose	b_o	45.62			3.26	0.83	3.45	0.83
	b_1	-135.51	λ_1	2460				
	b_2	1413.38	λ_2	2132				
	b_3	-679.18	λ_3	2332				
	b_4	-629.53	λ_4	1678				

Table 3.4: Calibration results for fresh leaf samples, SEC = standard error of calibration, Rc = correlation coefficient of calibration, SEP = standard error of prediction, Rp = correlation coefficient of prediction

using the same wavelengths as the dried leaf analysis (Table 3.4). A typical fresh leaf spectra with the locations of the wavelengths used in this method are shown in Figure 3-1.

The first wavelength used in the nitrogen calibration($2174nm$), is associated with a strong protein absorption feature and has a correlation coefficient of 0.81. Wavelengths close to $2170nm$ are also used in NIR equations used to predict nitrogen in dried, ground foliage and litter, and decomposed foliage (McLellan *et al.* 1991a, 1991b). Absorption at this wavelength is due to absorption by N-H bonds in leaf protein(Osborne and Fearn 1986; Murray and Williams 1987). Absorption bands at 2128 and $1712nm$ are associated with protein and C-H bonds, respectively (Osborne and Fearn 1986; Murray and Williams 1987). The equation using three wavelengths has an multiple correlation coefficient of 0.95.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

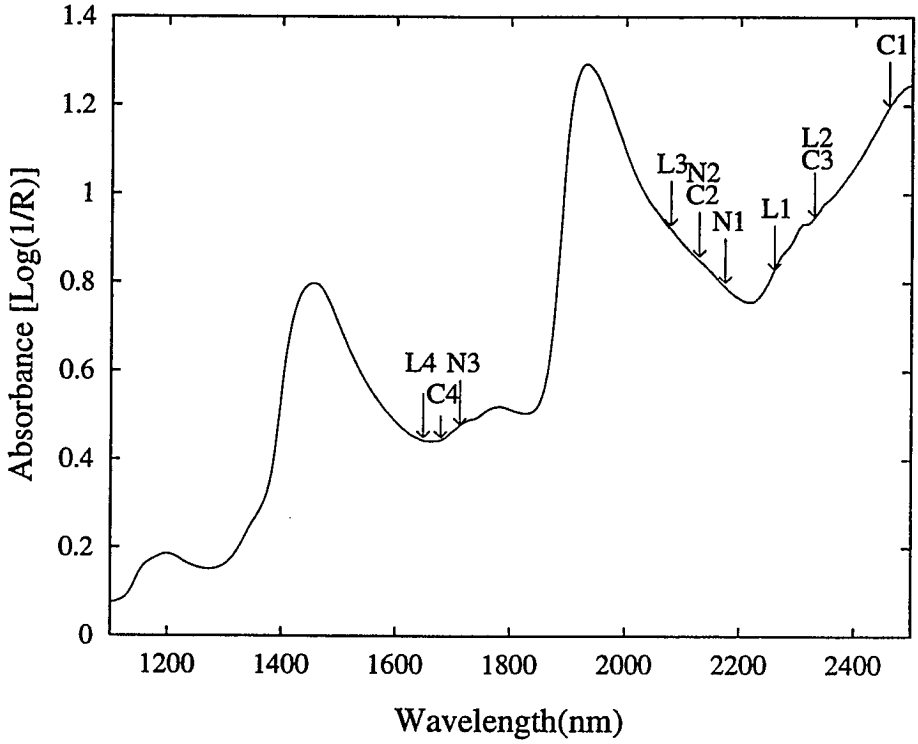


Figure 3-1: NIR spectra of fresh conifer needles showing locations of wavelengths used in calibration equations(nitrogen[N1-3], lignin[L1-4], cellulose[C1-4]

The first wavelength used in the lignin calibration equation, 2260nm, was identified by Himmelsbach *et al.* (1988) as a lignin absorption band. 2330, 2078 and 1648nm absorption bands are due to C-H, O-H, and C-H bonds, respectively (Osborne and Fearn 1986). This four term calibration equation has a correlation coefficient of 0.91. The six term equation derived by Wessman *et al.* (1988a) to predict lignin in dried, ground foliage used second derivative absorbance values in these same spectral regions (2270, 2327, 2078, 1654nm). Barton II *et al.* (1992) identify 2280, 2330, and 1678nm as absorption features correlated with lignin molecules.

Wavelengths chosen for the cellulose calibration, 2460, 2132, 2332, and 1678nm, can be attributed to absorption by C-H bonds present in leaf cellulose and other molecules. The correlation coefficient for this equation is 0.83. Absorption peaks

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

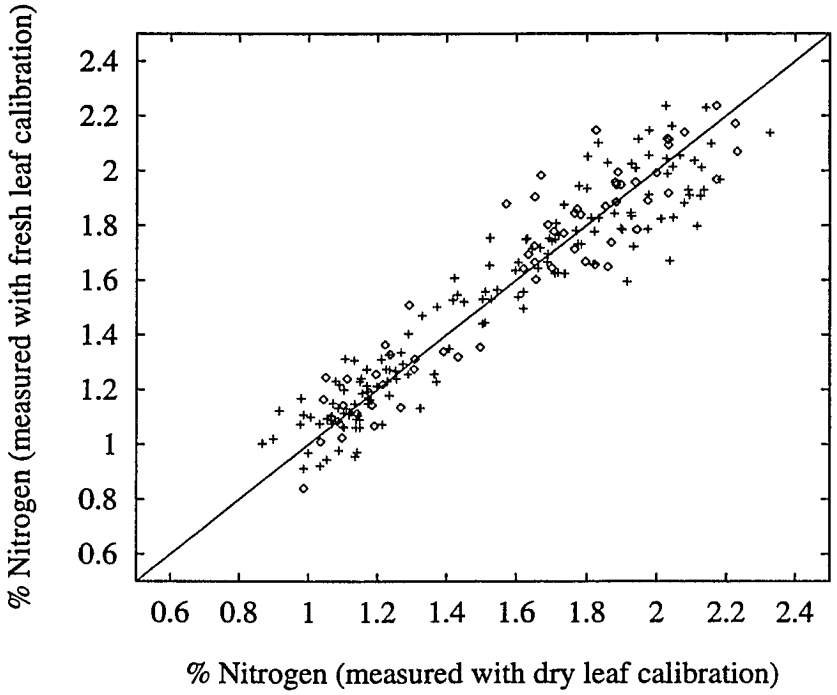


Figure 3-2: NIR predictions of percent nitrogen for fresh leaves vs dried ground leaves. x = calibration sample, ◇ = validation sample.

at 2330 and 2487nm have been identified as cellulose and starch features (Osborne and Fearn 1986). Shenk *et al.* (1979) and Norris *et al.* (1976) used 2148 and/or 1672nm to predict acid detergent fiber in forages.

Figures 3-2, 3-3, and 3-4 show the relationship between chemical concentration as determined by fresh leaf NIR analysis using the equations derived in this last analysis vs. measured values (NIR analysis of dried, ground sample).

To evaluate the precision of this method the four individual spectra of each sample were used to predict chemical concentration. The average coefficients of variation ($CV = \sigma \div < mean >$) of predicted values for the conifer and deciduous samples in this study are 1.2%, 1.00% and 0.8% for nitrogen, lignin, and cellulose, respectively. This variation includes the effect of both sample rotation and sample cell repacking. These values are similar to the variability of repeat measurements

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

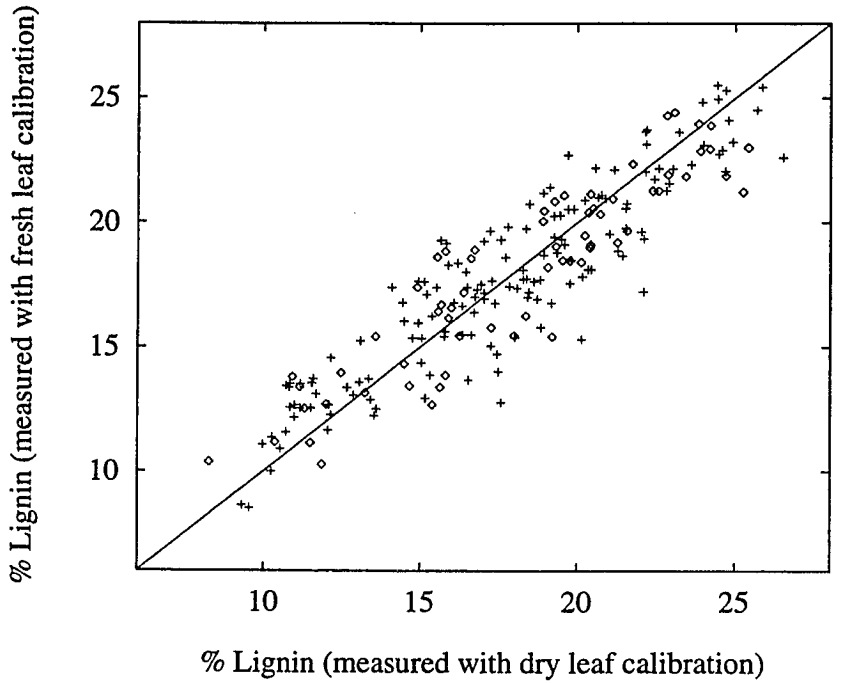


Figure 3-3: NIR predictions of percent lignin for fresh leaves vs dried ground leaves. x = calibration sample, ◇ = validation sample.

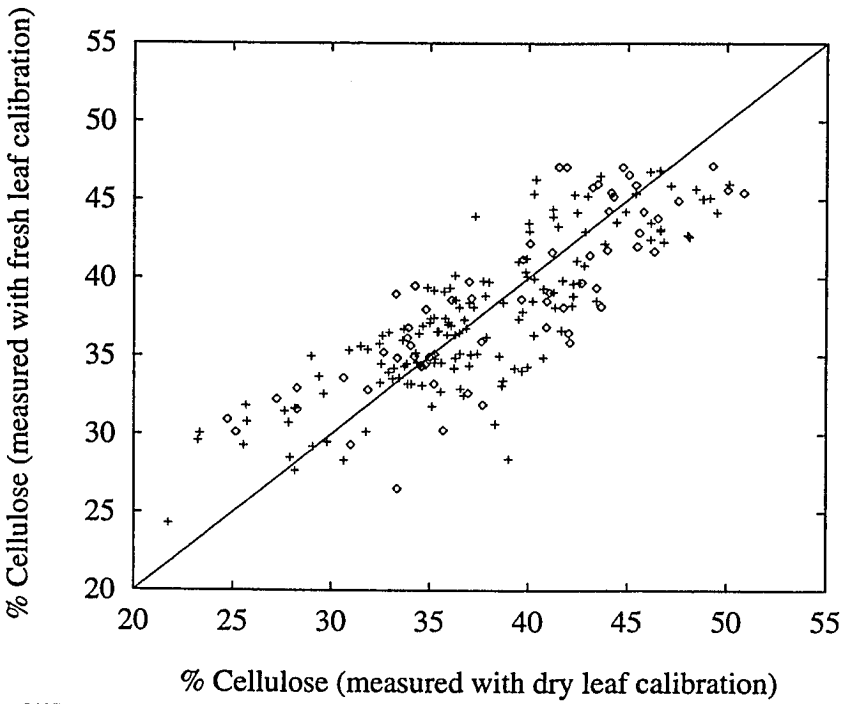


Figure 3-4: NIR predictions of percent cellulose for fresh leaves vs dried ground leaves. x = calibration sample, ◇ = validation sample.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

on dry, ground samples (1.42%N, 0.92%L, and 0.51%C). Therefore leaf restacking and sample cell rotation for fresh leaf samples does not decrease the precision of the predictions.

3.5 Summary

We have derived equations for the prediction of foliar nitrogen, lignin, and cellulose concentrations from fresh leaf NIR spectra. The wavelengths used for nitrogen(1712, 2128, and 2174nm), lignin(1648, 2078, 2260, and 2330nm), and cellulose (1678, 2132, 2332, and 2460 nm), are correlated with biophysical absorption features, and can be used to predict these constituents with correlation coefficients of 0.95, 0.91, and 0.83, respectively. These whole-leaf level relationships between chemical composition and NIR spectra suggest that information on biochemical content of foliage contained in dried ground materials is preserved in whole-leaf spectra. These relationships between fresh leaf reflectance spectra and leaf chemistry will be used as starting point in research to determine the chemistry of whole forest canopies. Spectral analysis of forest canopy chemistry with remotely sensed data will provide the means to make large scale remote sensing assessments of ecosystem processes such as nutrient cycling and carbon balance.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Chapter 4

THE STUDY OF FOREST ECOSYSTEMS THROUGH THE REMOTE SENSING OF CANOPY CHEMISTRY

4.1 Introduction

Measurements of nutrient cycling and photosynthesis are critical in assessing the exchange of greenhouse gases occurring between the soil, vegetation, and the atmosphere (Mooney *et al.* 1987; Steudler *et al.* 1989; Wofsy *et al.* 1993). Traditionally, such measurements have been made by time consuming field data collections, providing information on a very small scale. Remote sensing provides the opportunity to make regional scale measurements of forest ecosystem function.

Foliar chemical composition can be used to describe and model forest ecosystem processes such as nutrient cycling and carbon storage (Wessman *et al.* 1988b; Aber and Federer 1992). A number of field studies have shown a close relationship between the chemical composition of leaf and litter decomposition rates, thereby nutrient cycling rates (Melillo *et al.* 1982; Aber and Melillo 1982; McClaugherty *et al.* 1985; McClaugherty and Berg 1987). Foliar nitrogen is also closely related to the maximum photosynthetic rate in certain species (Field and Mooney 1986; Reich *et al.* 1992).

Regional estimates of carbon balance and nutrient cycling through remote sens-

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

ing, requires that field data be correlated with remotely sensed data and those relationships extrapolated to unsampled areas. A number of studies have investigated the relationships between canopy chemistry and remotely sensed data in a variety of forest ecosystems (Peterson *et al.* 1988; Wessman *et al.* 1988b; Johnson and Peterson 1991; Johnson *et al.* 1994; Matson *et al.* 1994). In these studies, NIR spectral data have been correlated with field measured foliar chemistry (i.e., nitrogen, lignin, starch). Data for these studies were acquired with the Airborne Imaging Spectrometer (AIS) and the Airborne Visible/Infrared Imaging Spectrometer (AVIRIS).

The success of remote sensing work depends upon accurate field data sampling. Seasonal variations in the foliar chemistry of a number of species have been observed (MacLean and Robertson 1981; Chapin III and Kedrowski 1983; Staaf and Stjernquist 1986; Matson *et al.* 1994) and must be fully understood in order for field data sampling to adequately represent conditions at the time of a remote sensing overflight.

The primary objective of this research is to determine how spectral data from AVIRIS is related to field measured canopy chemical composition, and to use spatial estimates of canopy chemistry to drive ecosystem models. We present examples of a carbon balance model (PnET model, Aber and Federer (1992)) driven by canopy nitrogen concentration and a simple linear model of nitrogen mineralization driven by canopy lignin concentration (Wessman *et al.* 1988b).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

4.2 Methods

4.2.1 Field Study Sites

The data used in this study were collected at the Harvard Forest, Massachusetts and Blackhawk Island, Wisconsin. Twenty study plots were located at each site, and were chosen to cover a wide range of species composition and to cover the widest possible range of foliar chemistry.

The Harvard Forest is located in Petersham, Massachusetts (Lat 42°32'N Longitude 72°11'W). The plots established at this site cover an area of approximately 5 x 10km. The species composition at this site is mixed hardwood (primarily oak and maple), conifer stands of red and white pine, norway spruce, larch and hemlock. The red pine, norway spruce and larch stands were planted while the hardwood, white pine, and hemlock stands are naturally occurring. There has been a long history of research at this site covering such aspects as litter decomposition, nutrient cycling, carbon balance, and trace gas exchange (Aber *et al.* 1990; Bowden *et al.* 1991; Aber *et al.* 1993; Wofsy *et al.* 1993)

Blackhawk Island, located in south-central Wisconsin (Lat 43°40'N Longitude 89°45'W) is a natural area containing a wide range of forest types including primarily sugar maple, basswood, oak, red and white pine, and hemlock. Blackhawk Island has been the site of a number of studies providing data on soils, litter decomposition, nutrient cycling, net primary production, and remote sensing (Nadelhoffer *et al.* 1982; Pastor *et al.* 1982, 1984; Wessman *et al.* 1988b)

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

4.2.2 Field Data Collection

Seasonal Chemistry Collection

In order to determine the seasonal variation of foliar nitrogen and lignin in conifer and deciduous species, preliminary data collections were made at approximately 3 week intervals during the 1989 (conifer) and 1990 (deciduous) growing seasons (1989: 30 June, 19 July, 7 August, 1 September, 8 October; 1990: 19 June, 10 July, 31 July, 27 August, 18 September, and 16 October). Foliage was collected from individual trees to assess the temporal variability in both foliar nitrogen and lignin. During each sampling, leaves were collected from three trees of each species. Each sample consisted of leaves from 3 different heights within the canopy. The samples were analyzed for nitrogen and lignin concentration (percent dry weight) using the NIR method of McLellan *et al.* (1991a).

Green Leaf Collections for AVIRIS Overflight

Green leaf samples were collected within 10 days of the AVIRIS overflights to determine the chemistry of each species on each plot (HF: 18-23 June 1992, BHI: 26-29 June 1992). On each plot we identified all dominant overstory species and selected 5 trees of each species from which green leaves were collected. Leaves were collected by shooting small branches from the canopy with a shotgun. Each sample consisted of leaves composited from several heights in the canopy. For needle-leaved samples, no separation was made between needles of different ages. The samples were sealed in ziplock bags and weighed within several hours of collection. The samples were

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

then oven dried at 70°C for 48hrs and reweighed. The fresh and dry sample weights were used to determine water content. After drying, the leaves were ground with a Wiley Mill to pass through a 1mm mesh screen.

Dried and ground leaves were analyzed for chemical composition. Cellulose and lignin were measured using a sequential extraction/digest method (TAPPI 1975, 1976; Effland 1977; McClaugherty *et al.* 1985; Newman *et al.* 1994). This method separates carbon compounds into nonpolar extractives (fats, waxes), polar extractives (starches, sugars, simple amino acids and polyphenols), acid digestible (cellulose), and acid insoluble (lignin) fractions. The CHN combustion method (Perkin-Elmer 2400) was used to determine carbon, nitrogen and hydrogen content of each sample (Page *et al.* 1982). A subset of samples were also analyzed for nitrogen concentration using a modified Kjeldahl method. The CHN and Kjeldahl methods produced similar results (Newman *et al.* 1994).

Litterfall Collection

Litter collection data were used to determine the species composition of the canopy at each plot. Ten litter baskets were randomly placed in each plot in early September. The litter was collected from deciduous sites through mid-December when litterfall was complete. Conifer litter was collected through the following May to capture both fall and spring litterfall. Litter was air-dried and sorted by species. All species were identified when possible, with leaf fragments and unidentifiable litter being classified as no-id. This no-id category averaged less than 1% of the litter by weight in each basket. The litter was then oven-dried at 70°C for 48hrs and

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

weighed. Deciduous litter weights were used as measured, conifer litter weights were multiplied by foliar retention time (one year of litterfall only represents a portion of the canopy biomass for a conifer species). Canopy level nitrogen and lignin concentrations were calculated as mean concentration per species (green leaf collection) weighted by foliar mass per species (litter collection) (Tables 4.1 and 4.2).

4.2.3 Remote Sensing Data

AVIRIS Data Description

The Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) was designed and built by NASA's Jet Propulsion Lab (JPL) to carry out high spectral resolution imaging of the Earth (Vane and Goetz 1988; Porter and Enmark 1987). Flying at an altitude of 20km on board an ER-2 aircraft, this instrument has a 20m spatial resolution and covers a swath of approximately 10km in width. A spatial image is collected by a cross track scanning mechanism (perpendicular to the direction of travel) and the forward motion of the aircraft. AVIRIS measures 224 contiguous spectral bands for each picture element (pixel) ranging from .4 to 2.4μm with a spectral resolution of 10nm (Vane *et al.* 1988). AVIRIS data are received from JPL with radiometrical corrections applied. These corrections convert raw AVIRIS digital numbers to radiance values for each pixel in units of $\mu Wcm^{-2}nm^{-1}sr^{-1}$ (Reimer *et al.* 1987).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Plot	Species	Nitrogen	Lignin	Water	Cellulose	Litter Biomass
		(%)	(%)	(%)	(%)	(g.ha-2.yr-1)
1	Red oak, red maple	2.02	25.02	63.69	40.11	2510.74
2	Red maple, red oak	2.02	20.09	63.29	36.65	2347.72
3	Red oak, red maple	2.23	25.68	62.80	39.46	2304.05
4	Sugar maple, red maple	2.18	18.79	64.21	39.51	2540.94
6	Larch	2.44	29.66	68.12	34.09	3151.77
7	Red Pine, norway spruce	1.25	26.75	51.28	38.92	1191.68
8	Norway spruce	1.25	25.69	60.40	38.96	2352.37
9	Hemlock	1.23	15.73	55.16	26.77	1819.66
10	White Pine, hemlock	1.41	22.91	55.16	36.25	1679.66
11	Red oak, red maple	2.23	23.53	64.69	39.27	2687.72
12	Norway spruce	1.35	23.69	58.62	41.79	2743.58
13	Norway spruce	1.22	25.26	60.27	40.83	2493.39
14	Red oak, red maple	2.04	23.35	61.62	35.74	2230.06
15	Red pine	1.06	26.17	55.26	39.07	3815.99
16	Red oak, red maple	2.32	22.17	62.28	38.78	2762.05
17	Red pine	1.21	25.91	56.03	39.74	3732.11
18	Red oak, red maple	2.33	20.92	63.57	39.72	1931.60
19	Red oak, red maple	1.94	23.32	59.04	35.07	2249.34
20	Red maple	1.86	19.20	57.97	33.03	2020.47
21	Red pine	1.04	25.53	54.42	38.19	3858.46

Table 4.1: Description of Harvard Forest plots. Dominant species are listed for each plot. Nitrogen, lignin, water, and cellulose are percent foliage dry weight as calculated from the green leaf and litter data for each plot.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Plot	Species	Nitrogen	Lignin	Water	Cellulose	Litter Biomass
		(%)	(%)	(%)	(%)	(g.ha-2.yr-1)
1	Sugar maple, basswood	2.32	19.35	60.56	41.57	2888.53
2	Basswood, sugar maple	2.61	20.11	61.26	44.17	3326.82
3	Sugar maple, red oak	2.35	20.59	61.40	41.91	3351.13
4	Sugar maple, red oak	2.49	19.72	60.08	42.55	2900.89
5	Red oak, poplar	2.39	23.67	58.65	40.72	2559.53
6	White pine, white oak	2.37	22.53	59.18	42.99	2870.53
7	Red oak, sugar maple	2.41	21.39	59.65	42.25	3228.06
8	Red oak, sugar maple	2.50	21.22	58.53	41.99	3076.46
9	Sugar maple, red oak	2.37	20.53	58.09	40.02	3165.93
10	White oak, red maple	2.48	21.42	57.84	41.22	2838.85
11	Sugar maple, red oak	2.40	20.33	59.73	43.06	3538.42
12	Red maple, red oak	2.37	22.84	56.95	40.02	3100.81
13	Red oak, white pine	2.29	25.72	56.43	43.71	2689.59
14	Red oak, red maple	2.18	23.81	39.81	55.12	3160.34
15	Red oak, red maple	2.38	24.12	56.75	41.19	3201.53
16	Red oak, white oak	2.27	23.48	56.38	40.76	2929.94
17	White pine, red oak	1.89	25.68	55.63	37.85	2535.27
18	White pine, red maple	1.91	25.86	55.89	37.92	2294.75
19	Red pine, white pine	1.49	25.77	56.21	39.15	1561.02
20	Red pine, white pine	1.49	26.33	56.27	39.06	1671.47

Table 4.2: Description of Blackhawk Island plots. Dominant species are listed for each plot. Nitrogen, lignin, water, and cellulose are percent foliage dry weight as calculated from the green leaf and litter data for each plot.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

AVIRIS Data Acquisitions

AVIRIS data were acquired for the Harvard Forest on 15 June 1992 (Figure 4-1). 1992 image data were acquired for Blackhawk Island on two dates. A flight on 12 June was cut short due to cloud conditions. However, the scene does contain all but the southern portion of Blackhawk Island. Weather conditions at the time of a 21 June overflight were more suitable, and calibration sites located to the south of the island were successfully observed (Figure 4-2). All 1992 Blackhawk Island analysis has been done with the scene of 21 June to allow for the greatest flexibility in atmospheric corrections.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

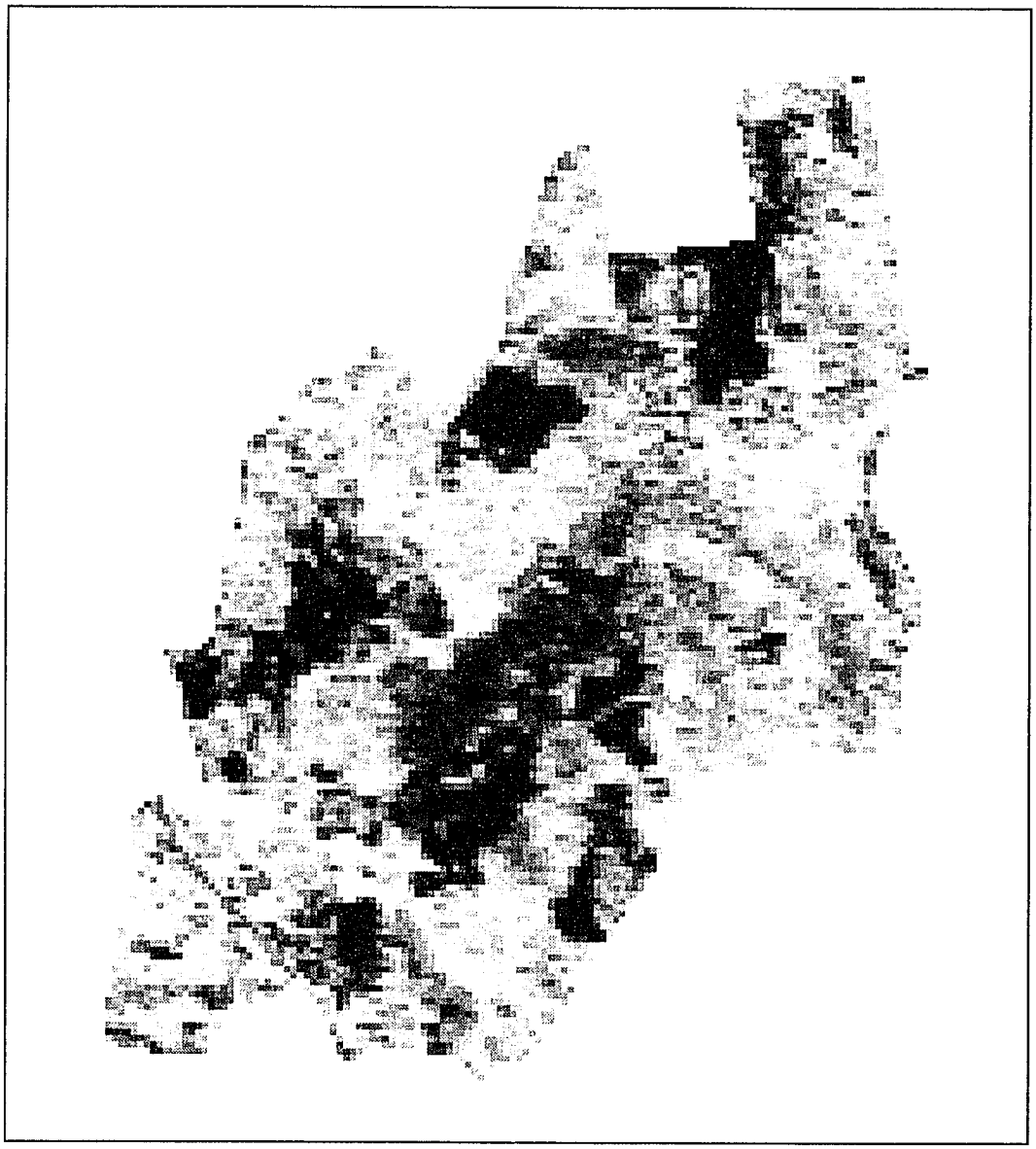


Figure 4-1: Harvard Forest: AVIRIS visible/infrared composite image. Red:2.20μm, Green:1.26μm, Blue:0.58μm

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

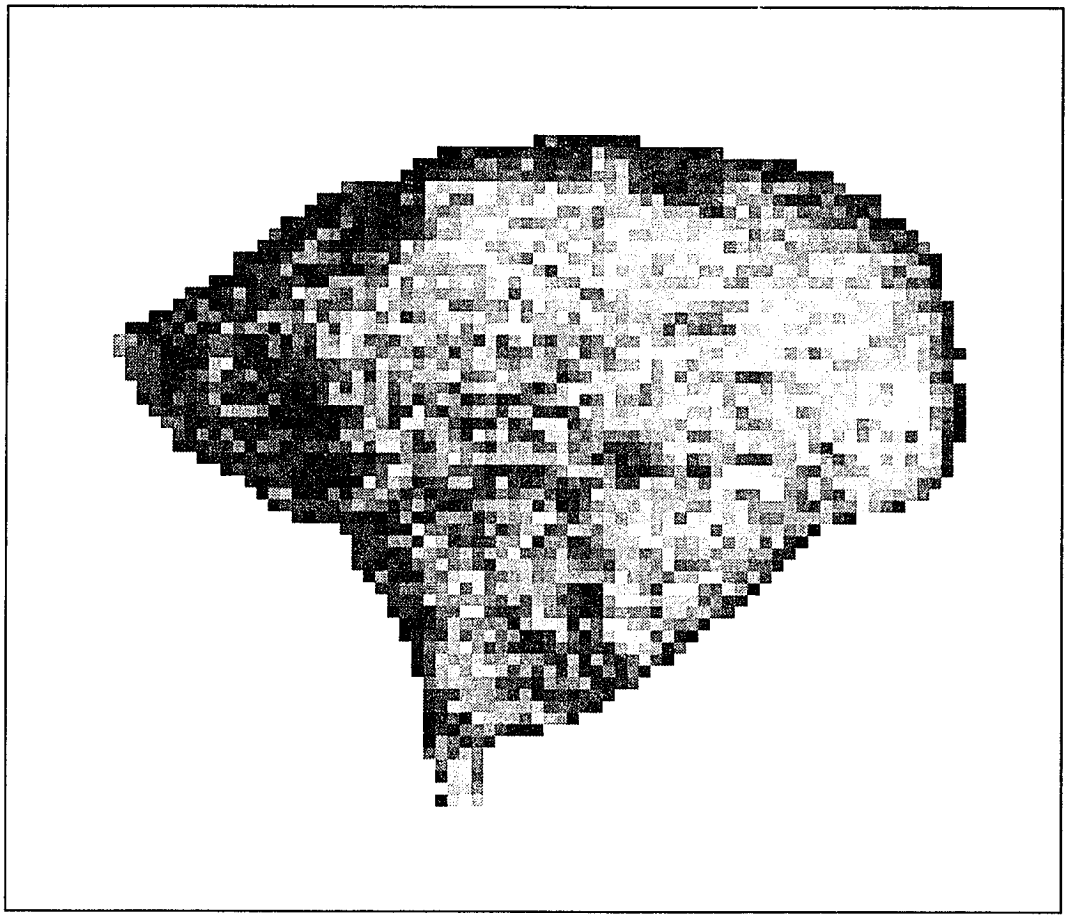


Figure 4-2: Blackhawk Island: AVIRIS visible/infrared composite image. Red:2.20μm, Green:1.26μm, Blue:0.58μm

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Ancillary Data Collection

Field Spectral Measurements

Ground based solar radiometric data were collected at the time of both Harvard Forest and Blackhawk Island overflights. Reflectance measurements of selected calibration sites within the Blackhawk Island scene were made during a period of several days surrounding the flight dates. These data were collected with a GER Mark IV spectroradiometer operated by JPL. These calibration sites were large, spatially uniform areas such as a golf course, water, and a sandpit. The water and sandpit were located south of Blackhawk Island and are present only in the 21 June scene.

Global Positioning System Data

Latitude and longitude of features in the Harvard Forest AVIRIS scene were determined with the use of a global positioning system (GPS). A Trimble Pathfinder Professional instrument was used to locate roads and study plots at Harvard Forest. Raw GPS data was collected as latitude/longitude and was then differentially corrected using base station data collected in Lexington, Massachusetts ($\approx$ 50 miles from Harvard Forest). Roads were located which could be identified in the AVIRIS scene for the purpose of geographic registration. Control points (primarily road intersections) distributed throughout the image were chosen for image registration. In most instances of registration the unknown coordinate system (image) is registered to the known coordinate system (latitude/longitude). However, in this study we registered the GPS data to the AVIRIS image. This registration allowed for AVIRIS

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

spectral data to be extracted from the original image cube of 614x512 pixels x 224 bands.

Atmospheric Corrections

Accurate transformations of AVIRIS imagery to reflectance at the canopy level must be made before any comparisons of temporal remote sensing data can be made. The accuracy of these corrections are crucial to the viability of remote sensing as an ecosystem monitoring tool. A number of atmospheric correction methods were evaluated for AVIRIS data in the context of NASA's Accelerated Canopy Chemistry Program. Several of these methods have been applied to AVIRIS data from Blackhawk Island and Harvard Forest. A complete review and comparison of the atmospheric correction algorithms used in this project can be found in Clark *et al.* (1993).

Data from the 21 June Blackhawk Island scene were atmospherically corrected with ground calibration data by Clark *et al.* (1993). This correction incorporated field reflectance spectra measured near Blackhawk Island at the time of the overflight. This method uses field, laboratory, and AVIRIS spectra measured at calibration sites to derive offsets and multipliers to transform AVIRIS radiance data to ground reflectance data.

Both Harvard Forest and Blackhawk Island scenes were also corrected using the ATREM atmospheric removal program of Gao *et al.* (1991, 1992). This method uses information within an AVIRIS radiance spectra to estimate atmospheric water vapor for each pixel which, in turn, is applied to a radiative transfer model to derive

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

ground reflectance. All 1992 ATREM corrected scenes are followed by a secondary correction based on the difference between a ground calibrated Blackhawk Island scene and the same ATREM corrected scene (Clark *et al.* 1993)(pers comm. K. Heidebrecht, R. Clark). Figure 4-3 shows atmospherically corrected spectra using both the Clark and ATREM methods.

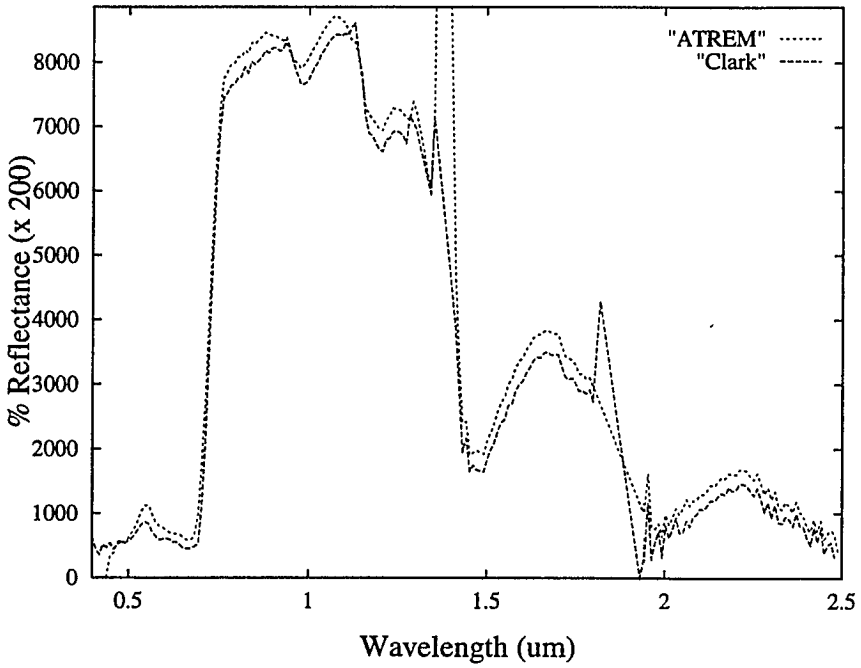


Figure 4-3: AVIRIS Spectra - reflectance calculated by Clark and ATREM methods

4.3 Data Analysis

4.3.1 Seasonal Variability in Foliar Chemistry

A one-way analysis of variance using the Bonferroni multiple comparison test was used to determine, for each species, between which sampling periods foliar chemistry differed significantly (Computing Resource Center 1992).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

4.3.2 Correlating AVIRIS Data with Canopy Chemistry Data

Relationships between AVIRIS data and field measured foliar chemical concentration were investigated with multiple linear regression analysis.

A first difference transformation was used on AVIRIS reflectance data:

$$\lambda_i' = < \lambda_{i+.5d} > - < \lambda_{i-.5d} >$$

where $< \lambda_i >$ is the mean reflectance value centered at λ_i for a spectral bandwidth of 30nm, and d is the distance between band centers (40nm). This first order difference transformation results in a spectrum in which peaks and valleys correspond with inflection points in the reflectance spectra.

Calibration bands were selected on a number of criteria: 1) bands of known absorbance for the biochemical of interest, 2) bands of highest AVIRIS signal:noise, and 3) bands least influenced by water absorption.

Regression equations were in the form:

$$\text{Concentration}(\%) = b_o + \sum_{i=1}^{n} b_i \lambda_i'$$

where λ_i' is the first difference reflectance value centered at λ_i and b_i is the regression fitting coefficient for that term.

4.3.3 Ecosystem Modeling

The PnET model (Aber and Federer 1992) originally developed to predict carbon balance for a single plot, was modified for this exercise to make spatially explicit

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

estimates. A primary driver for this model is foliar nitrogen concentration which is used to predict the maximum photosynthetic rate. We also used nitrogen concentration to estimate conifer vs hardwood species composition of each pixel in the image. If %N was greater than 2.2 the pixel was defined as all hardwood and the model was run with a canopy %N equal to the AVIRIS measured value. If the %N was less than 1.28, the pixel was defined as all conifer and run with red pine data (see Aber and Federer (1992)). For pixels between 1.28 and 2.2%N, two model runs were averaged, one using red pine, and the other using hardwood at 2.2% nitrogen. The final prediction for each pixel was a weighted mean of the pine and hardwood values, with the weighting a function of AVIRIS estimated %N:

$$\text{Hardwood weight} = \frac{\%N - 1.28}{2.2 - 1.28}$$

$$\text{Pine weight} = 1 - \text{Hardwood weight}$$

At Blackhawk Island, nitrogen mineralization rates were predicted using the simple linear model of Wessman *et al.* (1988b) which relates foliar lignin concentration to nitrogen mineralization rate. Before using this existing model, we transformed our 1992 lignin data to the same scale as those used by Wessman *et al.* (1988b). This correction is necessary because the chemical analysis for lignin varies between the two studies. The differences in lignin analysis occur in the ash content correction; in the data used by Wessman *et al.* (1988b) the lignin analysis was calculated with the assumption that all ash in the initial sample was present in the lignin fraction. In the 1992 lignin analysis, lignin concentration was calculated with the assumption that

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

ash was removed at each step in the extraction process in proportion to mass loss (Newman *et al.* 1994). We applied the linear equation developed by Wessman *et al.* (1988b) to the adjusted 1992 canopy lignin values to predict nitrogen mineralization rates at Blackhawk Island.

4.4 Results and Discussion

4.4.1 Seasonal Leaf Collections

Figures 4-4, 4-5, 4-6, and 4-7 show mean foliar nitrogen and lignin concentrations in hardwood and conifer samples at different sampling dates throughout the growing season. Error bars are shown for only one species per graph for clarity, however, these represent the typical variability for the chemical composition of the three samples collected for each species. Significant differences between sampling periods for each species were determined with one-way analysis of variance using the Bonferoni multiple seperability test. In softwood species, no significant variations in nitrogen concentration occurred between the different sampling periods (total variability was only 0.2%N during the five collection periods) (Figure 4-4). Of the three conifer species sampled, red pine shows the greatest variability in foliar lignin concentration, with a decrease occurring mid-season (Figure 4-5). In the red pine samples, all age needles were composited into a single sample, with approximately 40% of the needles in the first-year class. Lignin concentration drops with the expansion of new leaves, and then increases as these leaves begin to lignify later in the season (Rock *et al.* 1994). Although the same pattern of leaf expansion and lignification occurs

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

in the first year needles of hemlock and norway spruce, only 15-20% are first year needles and the influence on sample chemistry is not as strong as in the red pine.

No significant differences occurred in the nitrogen content of hardwood species between full leaf expansion and mid-September. Total variation in these species was only 0.2%N during this period (Figure 4-6). However, a significant drop in nitrogen concentration ($p < .05$) is observed between day 260 and day 295 in 4 of 6 hardwood species due to the retranslocation of nitrogen from the foliage prior to leaf senescence.

Lignin concentrations in hardwood species were significantly different between adjacent sampling periods for beech, gray birch, and hickory early in the growing season (Figure 4-7). However, after day 190, no significant changes occurred in lignin concentration.

Variability of foliar chemistry demonstrated by these data, indicates that, for certain species, field sampling must occur within a short period of time ($< \pm 3$ weeks) surrounding the acquisition of remote sensing data.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

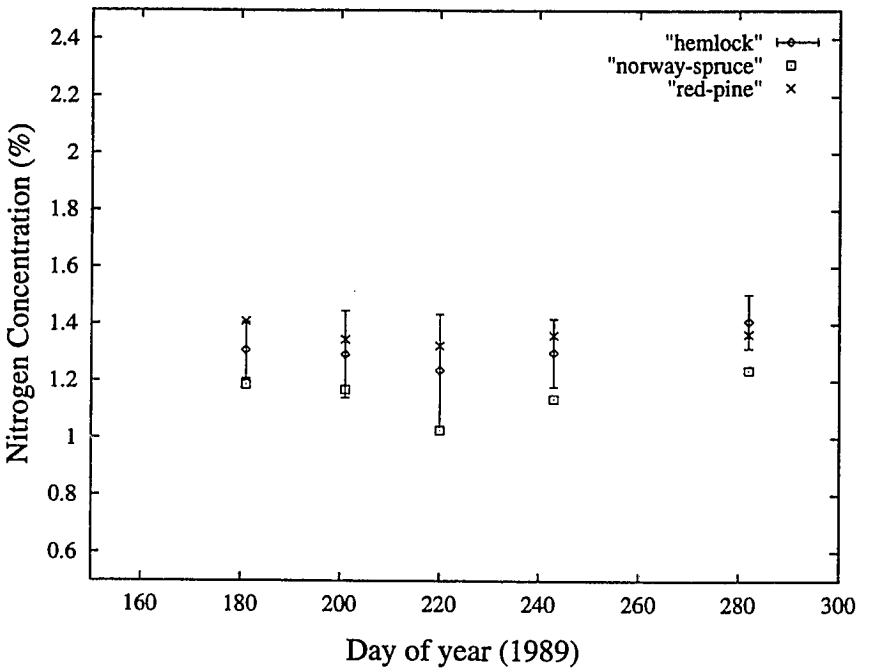


Figure 4-4: Seasonal variability in foliar nitrogen - conifer species. Chemistry was measured using the NIR method of McLellan *et al.* (1991a). Error bars are shown for only one species per graph for clarity, however, these represent the typical variability for the chemical composition of the three samples collected for each species.

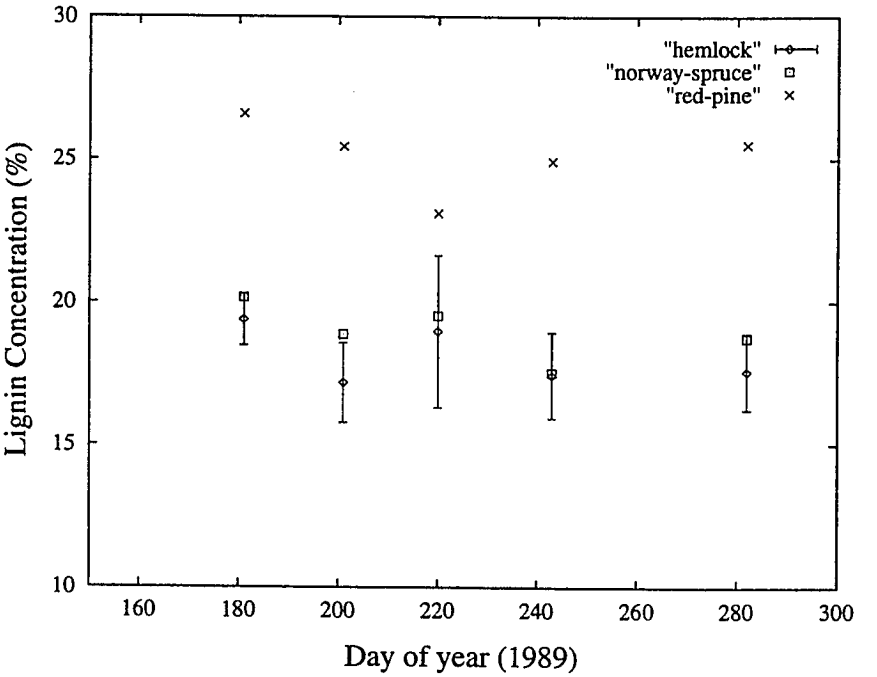


Figure 4-5: Seasonal variability in foliar lignin - conifer species

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

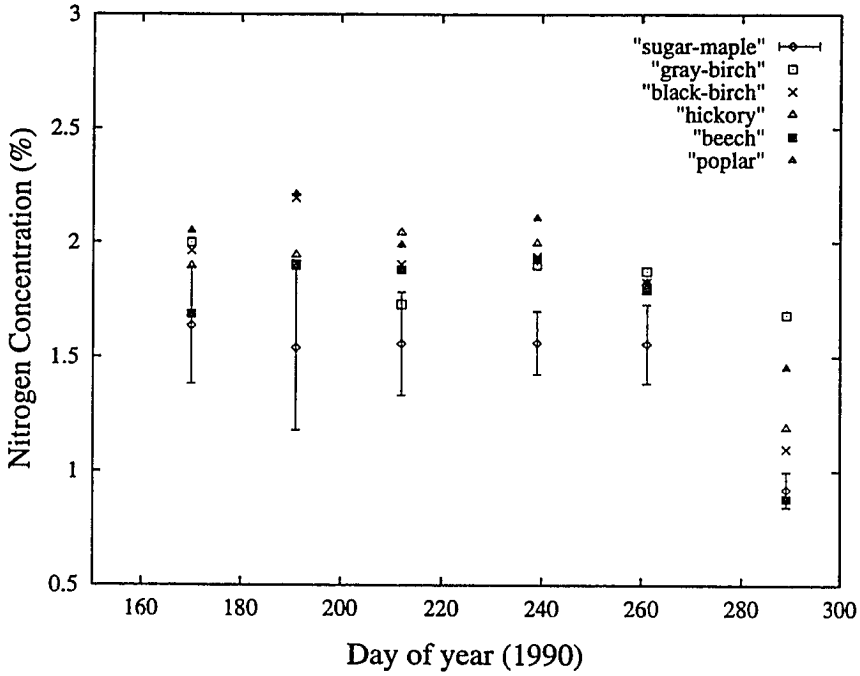


Figure 4-6: Seasonal variability in foliar nitrogen - deciduous species

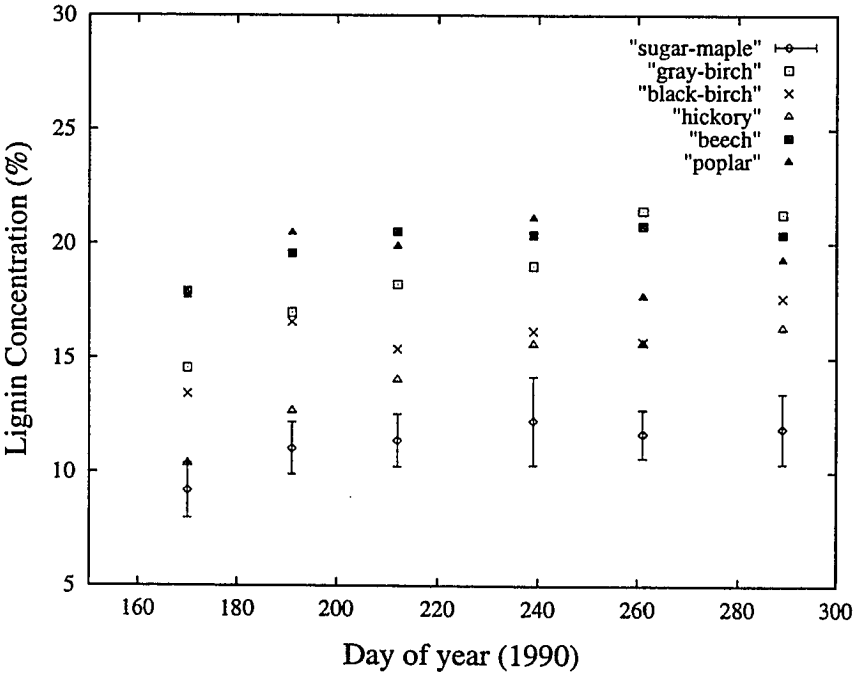


Figure 4-7: Seasonal variability in foliar lignin - deciduous species

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

4.4.2 Canopy Level Chemistry

Plot level data analysis at Blackhawk Island shows an east-west gradient in the concentration of several foliar constituents. This gradient is primarily due to changes in species distribution along an east/west soil and moisture gradient (Pastor *et al.* 1982). Nitrogen concentration (Figure 4-8) ranges from low (W) to high (E). Red and white pines on the west of the island have a lower nitrogen concentration than the oaks and maples throughout the remainder of the island. Highest nitrogen concentrations occur in mixed stands of sugar maple/basswood near the east end of the island. In contrast, total nitrogen (kg/ha, Figure 4-9) varies less across the island since multiple year foliar retention in the low nitrogen pines results in higher foliar biomass than deciduous species, and a more even distribution of nitrogen *content* across the island.

Carbon fraction concentrations vary across the island, with lignin values ranging from a high of 26% (W) to a low of 19% (E) (Figure 4-10). Cellulose concentrations (Figure 4-11) are highly variable on each plot. However, the *total* concentration of insoluble carbon compounds (cellulose + lignin, Figure 4-12) is relatively constant across the island, indicating a difference in the allocation patterns of carbon to structural molecules. Water fraction varies only slightly across the island (Figure 4-13), with concentrations slightly lower in the red and white pines, intermediate in oaks, and highest in sugar maples.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

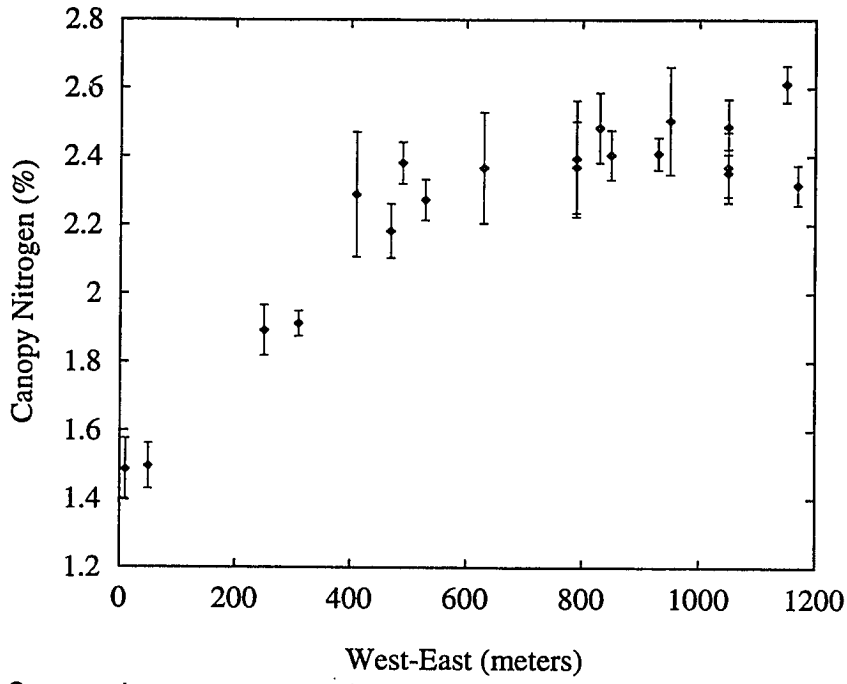


Figure 4-8: Canopy nitrogen concentration vs east-west gradient location at Blackhawk Island. Points represent mean values for nitrogen concentration calculated from litter and green leaf chemistry data for 10 litter baskets on each plot. Error bars represent ± 1 standard deviation.

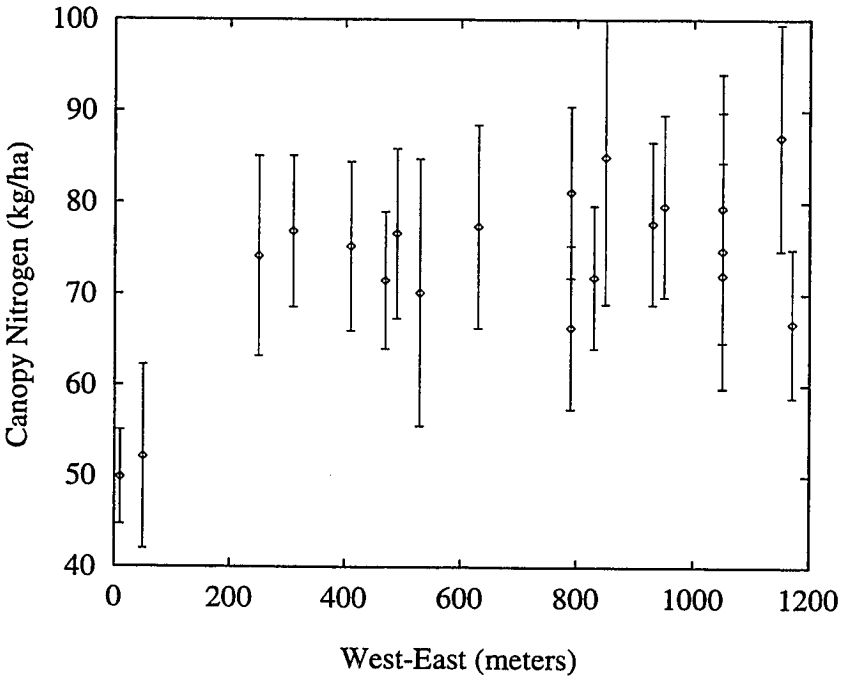


Figure 4-9: Total canopy nitrogen vs east-west gradient location at Blackhawk Island

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

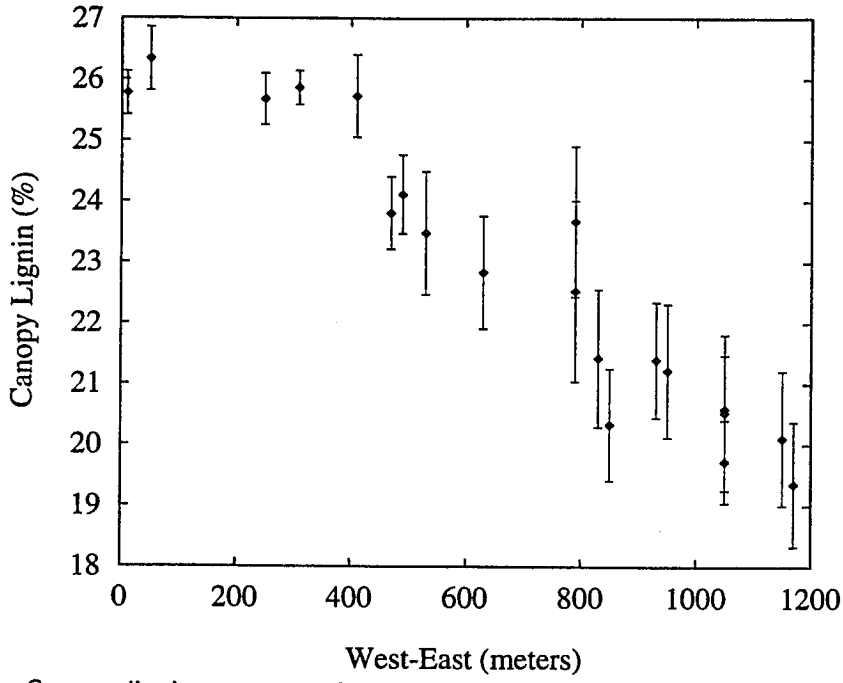


Figure 4-10: Canopy lignin concentration vs east-west gradient location at Blackhawk Island

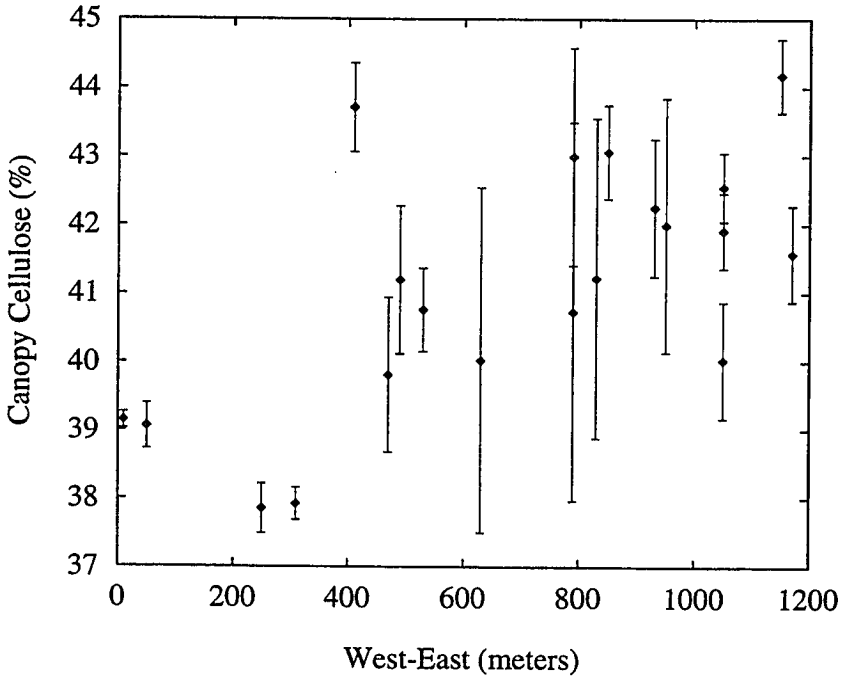


Figure 4-11: Canopy cellulose concentration vs east-west gradient location at Blackhawk Island

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

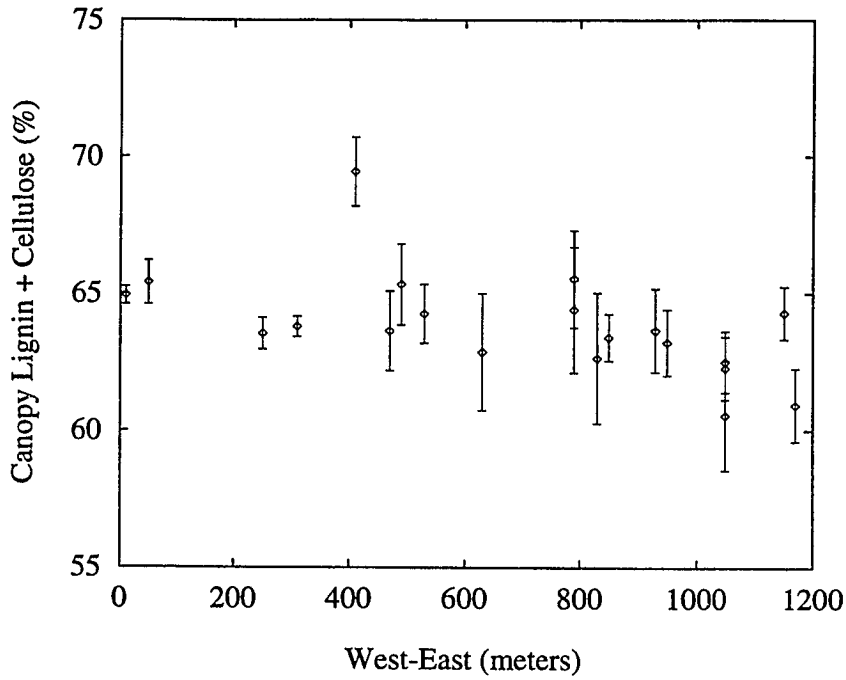


Figure 4-12: Canopy lignin + cellulose concentration vs east-west gradient location at Blackhawk Island

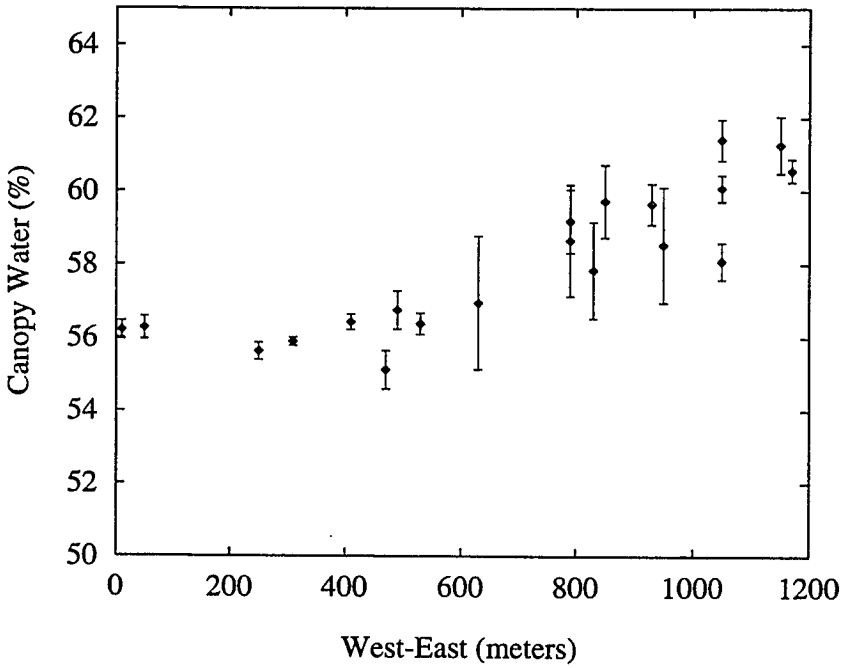


Figure 4-13: Canopy water concentration vs east-west gradient location at Blackhawk Island

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

4.4.3 AVIRIS and Field Data Correlations

The initial analysis of field and remote sensing data was done for each site (Blackhawk Island and Harvard Forest) individually. In this analysis, the AVIRIS data from twenty plots at each site were correlated with the field data. The resulting equations were then used to predict canopy chemistry at the other site to test the generalizability of the relationships. A further analysis of the data combined all 40 plots from the two study sites.

Harvard Forest

A two-term equation predicting nitrogen was developed between the AVIRIS first difference reflectance data and field measured nitrogen at Harvard Forest (Table 4.3). The two bands used in this equation are centered at 750 and 2140nm. Absorption in the 700nm region of the spectrum is related to foliar chlorophyll concentration (Gates *et al.* 1965). Chlorophyll content in foliage is highly correlated with total protein, and hence total nitrogen content (Field and Mooney 1986). A previous study by Rock *et al.* (1988) has shown that the slope of both laboratory and remotely sensed spectra in this red-edge region is sensitive to chlorophyll concentration. Absorption in the spectral region from 2110-2200nm has also been attributed to N-H bonds in amino acids and proteins (Osborne and Fearn 1986).

A four term equation relating AVIRIS data to canopy lignin used bands in the range of 1660 to 2280 nm (Table 4.3). Absorption in this region has been attributed to a number of different molecular bonds; 1620-1685nm: C-H aromatic, 1740nm: C-H and O-H, 1900nm: O-H C-O combination, 2280nm: C-H (Osborne

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

and Fearn 1986; Murray and Williams 1987; Curran 1989). Validations of the calibration equations were assessed by an iterative cross-validation method in which each sample in turn was dropped from the calibration process and predicted from the resulting equation (Mark and Workman 1991). These cross calibration results show that the standard error of prediction for samples not included in the calibration are only slightly higher than the standard errors of calibration.

Constituent	Coefficient		Wavelength		SEC	R^2	SECV
Nitrogen	b_o	0.4568			0.19	0.87	0.23
	b_1	0.0009	λ_1	750			
	b_2	-0.0016	λ_2	2140			
Lignin	b_o	33.4107			1.99	0.70	2.38
	b_1	0.1485	λ_1	1660			
	b_2	0.0268	λ_2	1740			
	b_2	-0.0005	λ_2	1900			
	b_2	-0.0349	λ_2	2280			

Table 4.3: AVIRIS calibration equations - Harvard Forest. Best calibration equation using only 20 plots from Harvard Forest

Blackhawk Island

The best relationship between AVIRIS data and field measured canopy nitrogen at Blackhawk Island used first difference reflectance bands at 950 and 2290nm (Table 4.4). Absorption at 2294 has been attributed to a combination band of N-H and C=O in amino acid by Osborne and Fearn (1986). The lignin equation developed in this analysis used bands at 790 and 1700nm. Osborne and Fearn (1986) assign absorption at 790 and 1685nm to aromatic structures, which are found in abundance in lignin molecules.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

4.4.4 Cross Site Predictions

The generalizability of the equations developed above for Harvard Forest and Blackhawk Island were tested by making cross-site predictions (Table 4.5). All cross-site predictions produced poor results indicating that the spectral and/or field information for each of the two study sites did not represent the other site. This difference may be due, in part, to the fact that 3 of the 4 equations used in the cross-site predictions use wavelengths in the spectral region with the lowest signal:noise ($\geq$ 2000nm).

4.4.5 Combined Site Calibration

Data from both Harvard Forest and Blackhawk Island (40 plots) were combined for the final lignin and nitrogen calibrations (Table 4.6). The band at 783nm is relatively close to the band at 750 used in the Harvard Forest calibration which is related to chlorophyll absorption. The band centered at 1640nm is a first overtone of a N-H absorption band (Murray and Williams 1987).

Absorption at 1660nm is related to absorption overtones of unsaturated or phenolic carbon-carbon bonds which are abundant in lignin molecules (Murray and Williams 1987). The three shorter wavelengths used in this equation correspond to a region of high absorbance observed in the laboratory spectra of lignin. The relationships between AVIRIS predicted and field measured nitrogen and lignin concentrations for the forty calibration plots are shown in Figure 4-14 and 4-15.

These equations, based on calibration pixels within the images, were then applied to all pixels in the images, yielding spatial estimates of foliar and nitrogen and lignin

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

concentrations at the canopy level for Harvard Forest (Figures 4-16 and 4-17), and Blackhawk Island (Figures 4-18 and 4-19). In order to use this type of prediction on a large scale with repeat coverage it will be necessary to develop calibration equations which will work on *multiple* scenes without the collection of field calibration data for each scene.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Constituent	Coefficient		Wavelength		SEC	R^2	SECV
Nitrogen	b_o	0.8608			0.13	0.85	0.15
	b_1	-0.0042	λ_1	950			
	b_2	-0.0007	λ_2	2290			
Lignin	b_o	31.65			0.78	0.90	0.85
	b_1	-0.0569	λ_1	790			
	b_2	-0.0263	λ_2	1700			

Table 4.4: AVIRIS calibration equations - Blackhawk Island. Best calibration equation using only 20 plots from Blackhawk Island

		Prediction Site			
Calibration Site	Constituent	Harvard Forest		Blackhawk Island	
		R^2	SEP	R^2	SEP
Harvard Forest	nitrogen	–	–	0.83	0.27
Harvard Forest	lignin	–	–	0.27	3.87
Blackhawk Island	nitrogen	0.75	1.32	–	–
Blackhawk Island	lignin	0.01	4.33	–	–

Table 4.5: AVIRIS cross-site prediction error

Constituent	Coefficient		Wavelength		SEC	R^2	SECV
Nitrogen	b_o	0.5292			0.18	0.87	0.19
	b_1	0.0008	λ_1	783			
	b_2	0.0035	λ_2	1641			
Lignin	b_o	33.8706			1.43	0.77	1.64
	b_1	0.1043	λ_1	627			
	b_2	0.0049	λ_2	755			
	b_2	-0.0493	λ_2	822			
	b_2	0.0519	λ_2	1661			

Table 4.6: AVIRIS combined site calibration. Equations developed with the data from all 40 Harvard Forest and Blackhawk Island plots.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

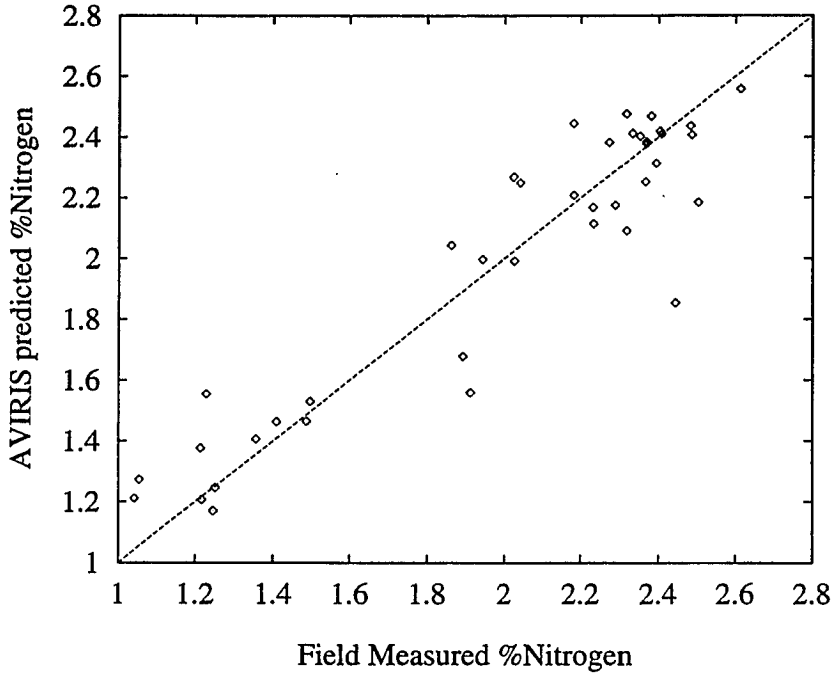


Figure 4-14: AVIRIS predicted canopy nitrogen concentration vs field measured canopy nitrogen - all calibration plots included (n=40)

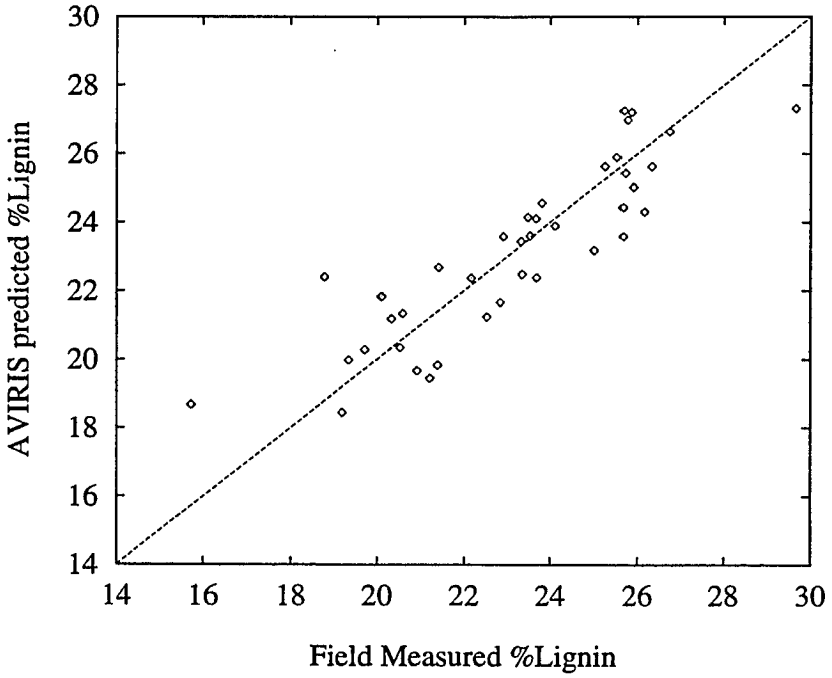


Figure 4-15: AVIRIS predicted canopy lignin concentration vs field measured canopy lignin - all calibration plots included (n=40)

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

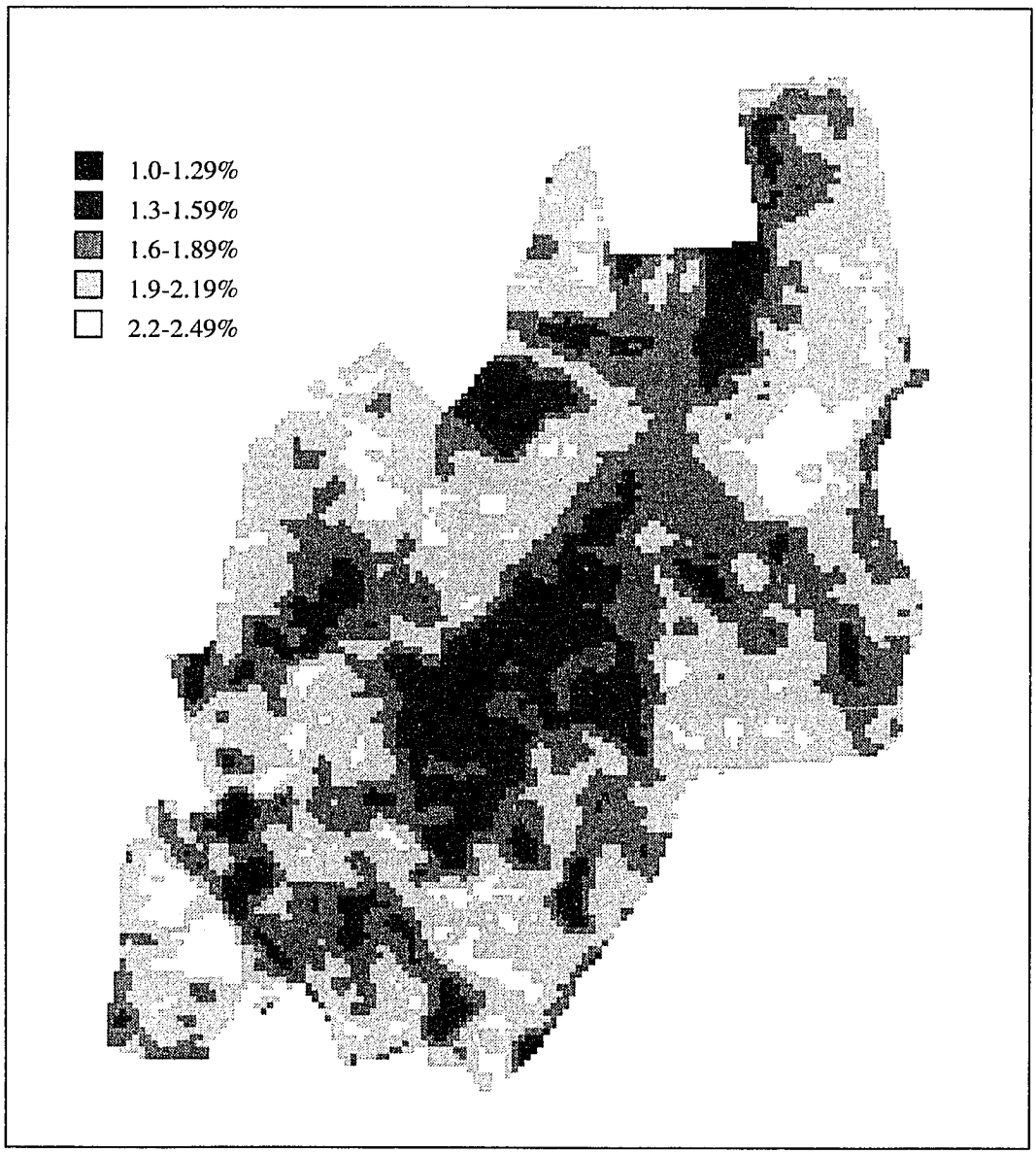


Figure 1-16: Harvard Forest - AVIRIS predicted canopy nitrogen concentration

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

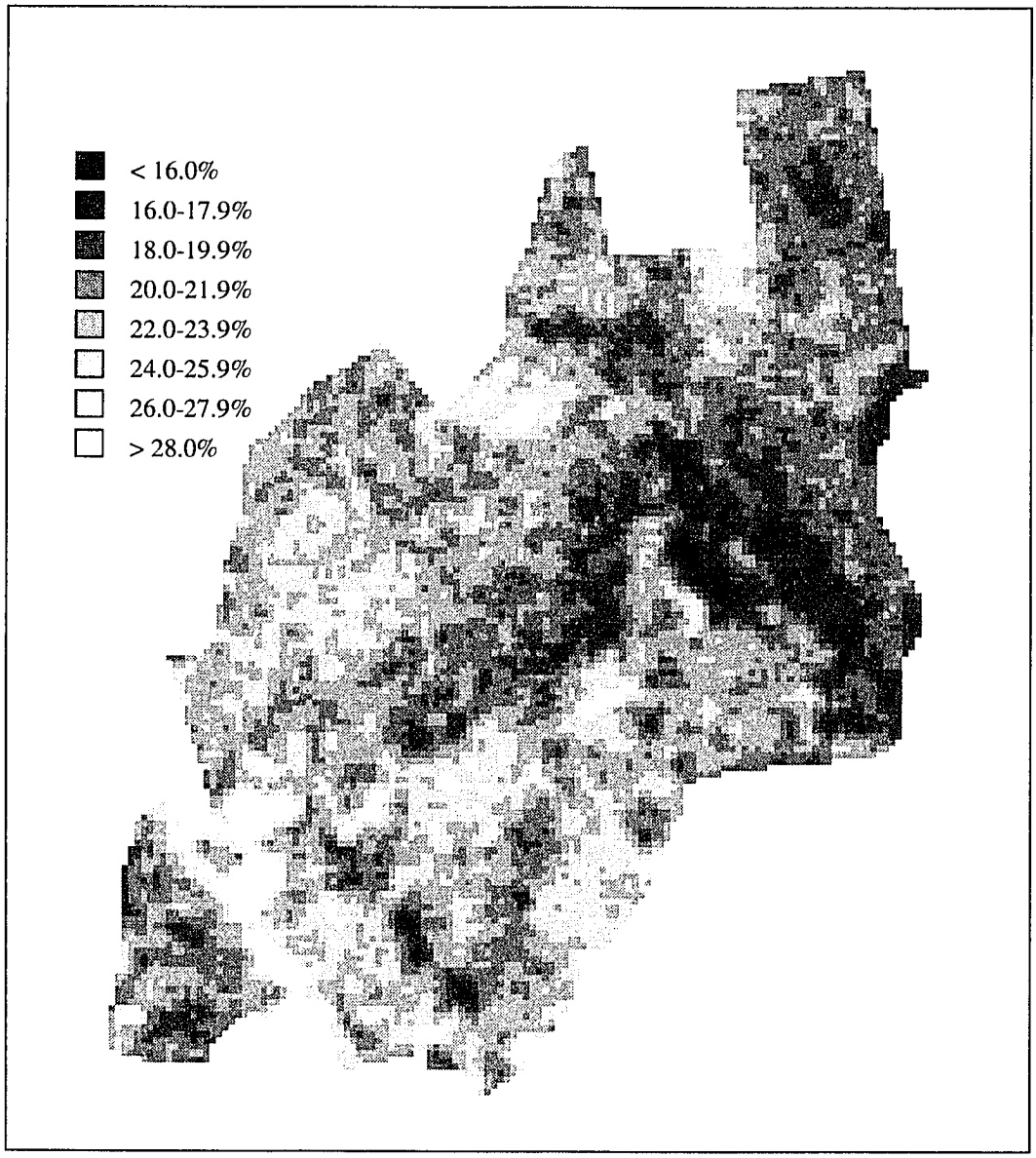


Figure 1-17: Harvard Forest - AVIRIS predicted canopy lignin concentration

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

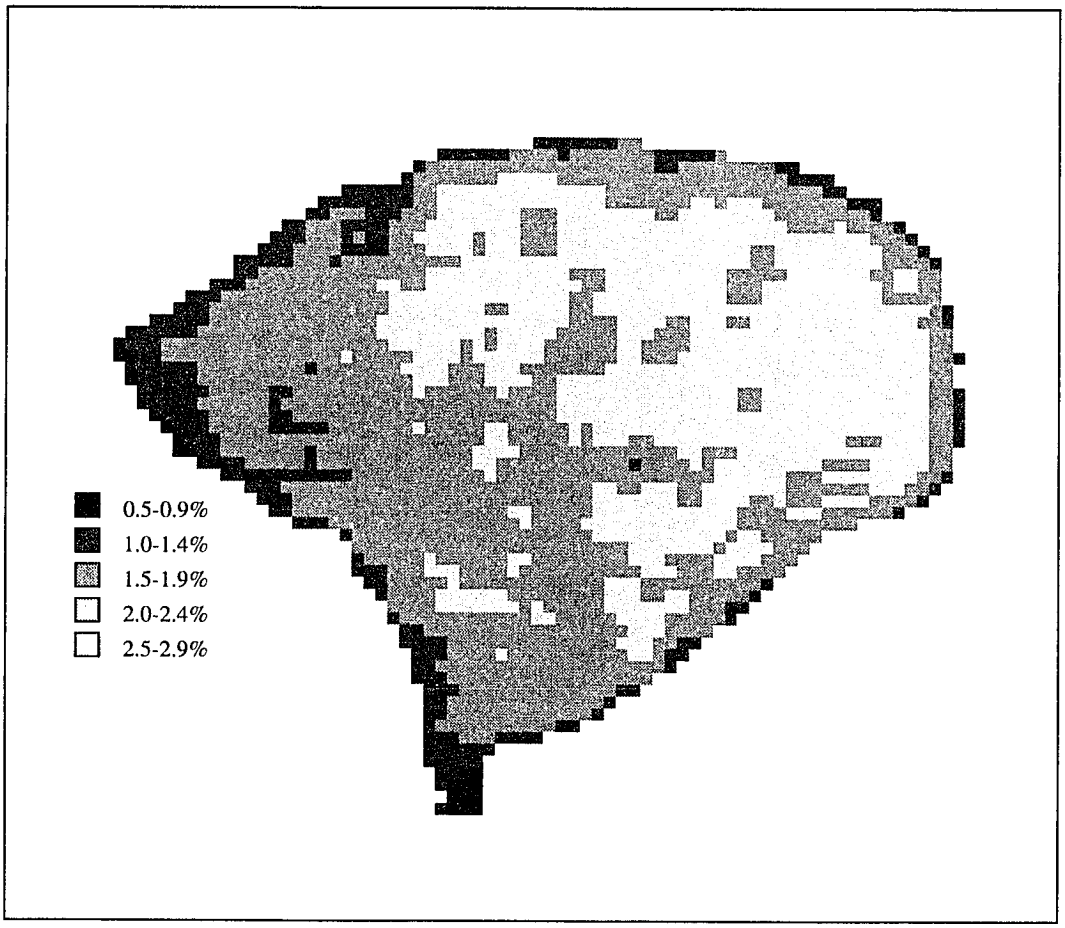


Figure 4-18: Blackhawk Island - AVIRIS predicted canopy nitrogen concentration

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

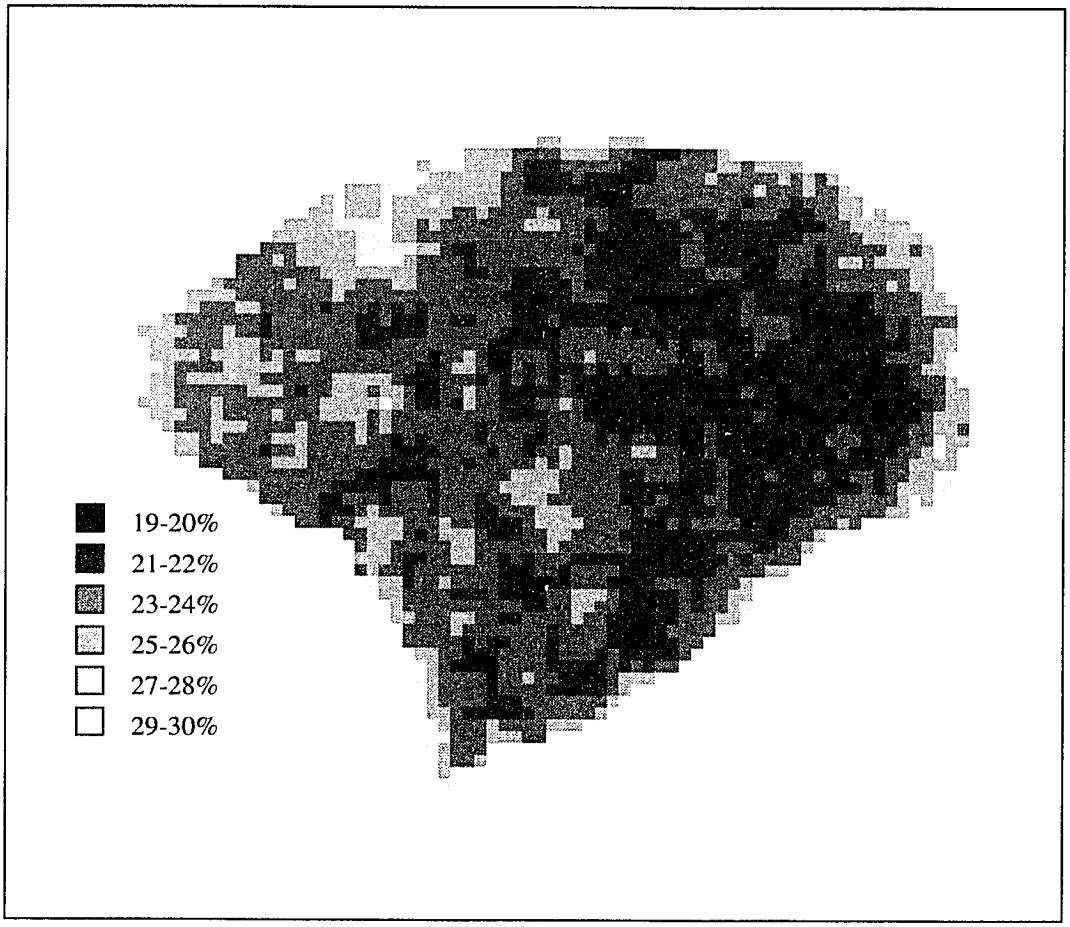


Figure 1-19: Blackhawk Island - AVIRIS predicted canopy lignin concentration

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

4.4.6 Modeling Ecosystem Processes with AVIRIS Derived Canopy Chemistry

AVIRIS predicted nitrogen and lignin have been used as input data for two models of ecosystem processes.

Previous research at Blackhawk Island has demonstrated a very strong (R^2=.96, n=7, $p < .001$) relationship between canopy lignin concentration and annual net nitrogen mineralization, or nitrogen cycling (Wessman *et al.* 1988b). This relationship has been used with remote sensing data from a low-elevation airborne platform to produce a verified map of nitrogen mineralization for Blackhawk Island (Wessman *et al.* 1988b). Using 1992 AVIRIS derived canopy lignin concentration as input to this model, we derived a map similar to that of Wessman *et al.* (1988b) showing the spatial variability in nitrogen mineralization rates on Blackhawk Island (Figure 4-20).

At the Harvard Forest, a model of monthly carbon balances (PnET) driven largely by foliar nitrogen concentrations has been validated against monthly carbon balance data obtained by eddy-correlation methods (Aber and Federer 1992). Using an image of foliar nitrogen concentrations at the Harvard Forest as input to this model, an estimate of net ecosystem carbon exchange is produced for the entire research site (Figure 4-21). The accuracy of this model may be improved by increasing the detail of the species map used as input. Chapter 5 discusses the potential for deriving species identification from AVIRIS data. Improvements in the species input variable will allow for more variability in conifer stands due to differences in

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

leaf area index and foliar retention time between conifer species. At the present time, field measurements of carbon balance are being made at Harvard Forest with eddy correlation methods. These field measurements will provide important data for the validation of carbon balance modeling derived from remotely sensed canopy chemistry.

4.5 Conclusions

Calibration equations relating AVIRIS spectral data to field measured canopy chemistry can be used to make spatially explicit estimates of canopy nitrogen and lignin within entire AVIRIS scenes. These estimates have been made for both Harvard Forest, Massachusetts and Blackhawk Island, Wisconsin. The subsequent application of these canopy chemistry estimates in ecosystem models adds an important spatial dimension to estimates of forest ecosystem carbon balance and nutrient cycling. The further study of these data, and similar datasets, will be used to develop more generalizable calibration equations, addressing such issues as variability between scenes due to atmospheric conditions and forest species composition. Establishing a baseline of forest ecosystem function, and monitoring changes which may occur in the future, are crucial components in understanding the role of forests in global biogeochemical cycles.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

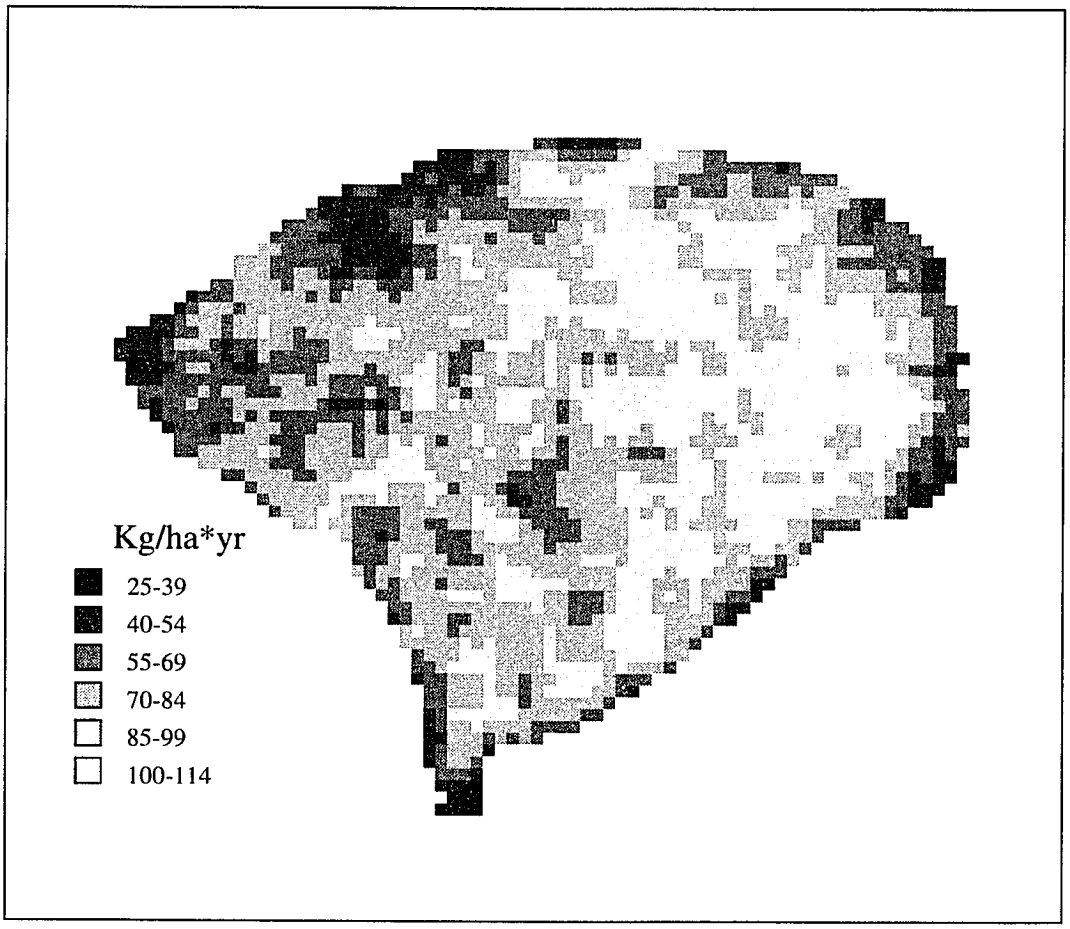


Figure 4-20: Nitrogen mineralization predicted from AVIRIS measured canopy lignin

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

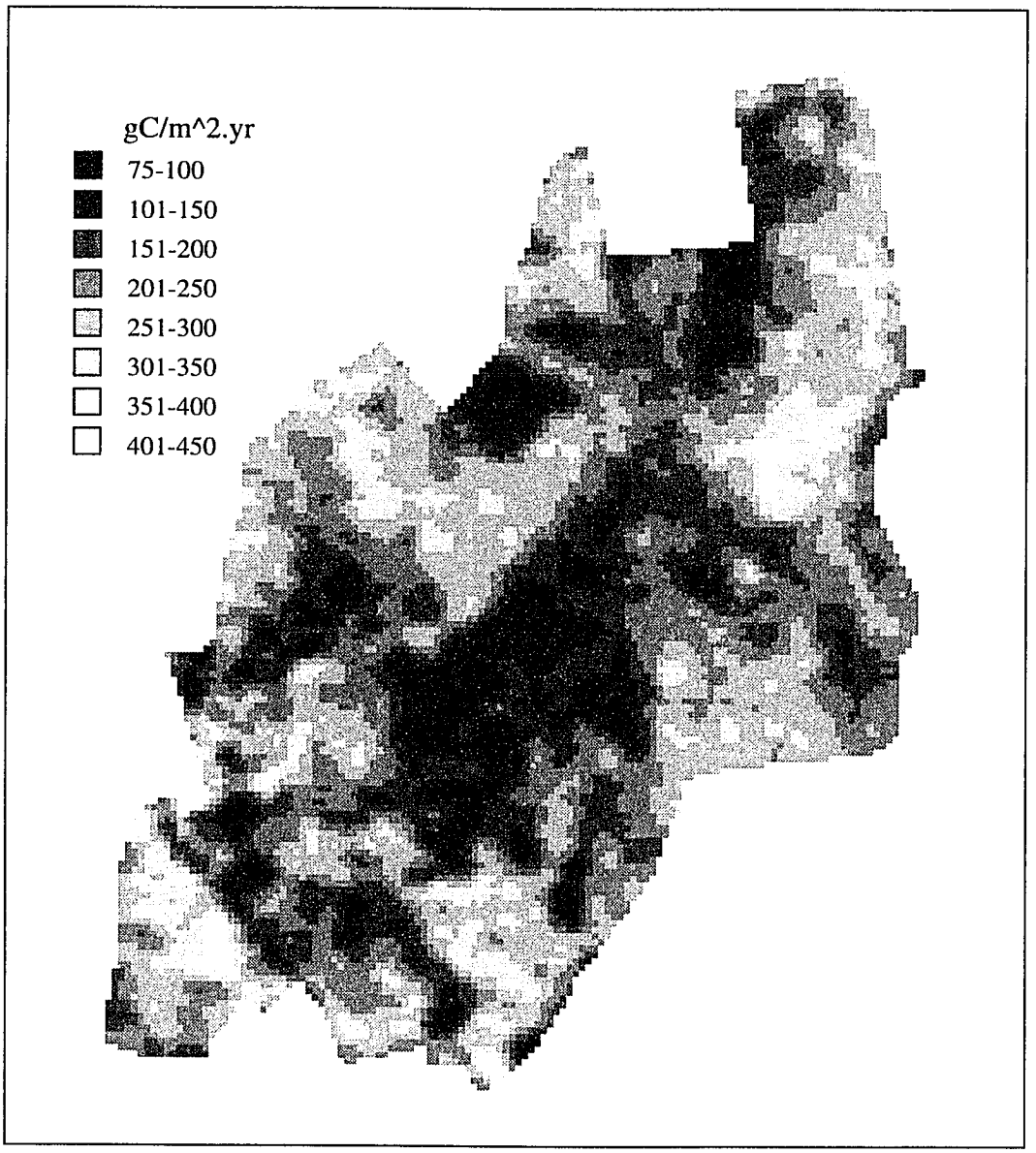


Figure 4-21: Harvard Forest - net ecosystem productivity predicted with PnET carbon balance model

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Chapter 5

DETERMINING FOREST SPECIES COMPOSITION USING HIGH SPECTRAL RESOLUTION REMOTE SENSING DATA

5.1 Introduction

Accurate species identification of forest stands is important in a number of scientific disciplines. Species identification via remote sensing will be valuable in monitoring any gradual changes in species distribution in response to changing climatic conditions - a scenario which has been predicted by Davis *et al.* (1986), Bradshaw and McNeilly (1991), Cramer and Leemans (1993), and Solomon and Cramer (1993). It is important that a baseline be established upon which to monitor such changes in species distribution.

Both forest and crop species inventory can be enhanced by remote sensing. Existing methods for estimating species distribution are limited to small scale field surveys and remote sensing. Remote sensing of forest cover has been used to identify broad categories, for example, conifer vs deciduous stands (Nelson *et al.* 1985; Shen *et al.* 1985; Hodgson *et al.* 1988; Lathrop *et al.* 1994). Instruments used for land cover identification include the Landsat Thematic Mapper(TM) and Multispectral Scanner(MSS), the airborne Thematic Mapper Simulator(TMS), SPOT and the

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Advanced Very High Resolution Radiometer(AVHRR). A number of studies have used these same instruments to classify forest type at the species level with varying degrees of success (Skidmore 1989). Species classifications have also been made with an airborne multispectral scanner (Rohde and Olson Jr 1972), and infrared video imagery (Everitt *et al.* 1987) The data from these instruments is limited both spatially and spectrally in contrast with newer instruments such as the Airborne Visible/ Infrared Imaging Spectrometer(AVIRIS).

The primary goal of this research project was to investigate the application of high spectral resolution remote sensing imagery of the forest canopy for the identification of species composition, using spectral regions correlated with the chemical composition of foliage.

In previous work we have successfully used data from AVIRIS to identify the nitrogen and lignin concentration in forest canopy foliage (Chapter 4). We further this research by relating these AVIRIS products to the identification of forest species composition.

5.2 Methods

5.2.1 Study Site

The study site for this project is the Prospect Hill tract at the Harvard Forest, in central Massachusetts (Latitude 42°32'N Longitude 72°11'W) (Figure 5-1). This 400 hectare research site contains a combination of natural hardwood, mixed hardwood/conifer, hemlock, and white pine stands as well as red pine and norway spruce

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

plantations.

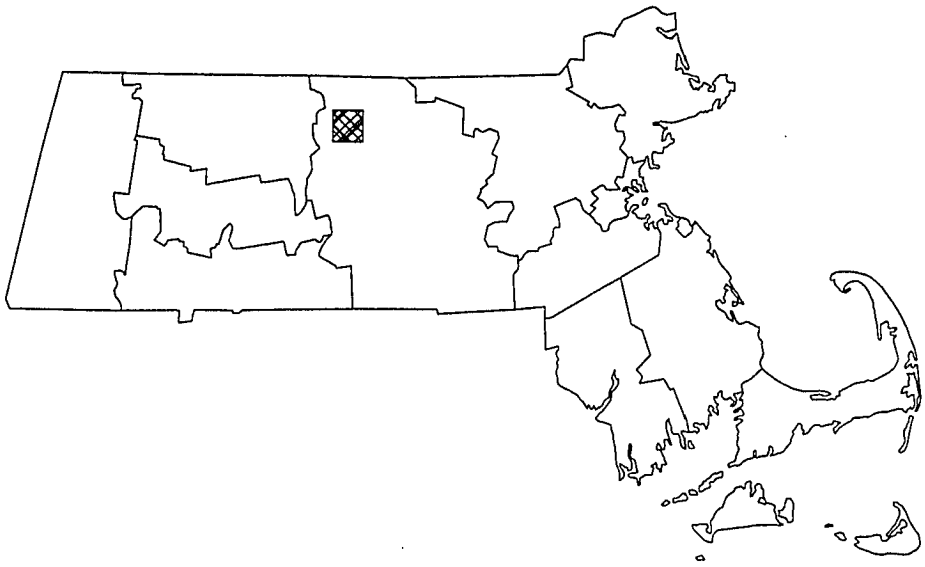


Figure 5-1: Location of Harvard Forest study site, Petersham, Massachusetts. (Latitude 42°32'N Longitude 72°11'W)

5.2.2 Foliage Collection

Leaf samples were collected at the Harvard Forest in June 1992 in support of a NASA campaign (Accelerated Canopy Chemistry Program) directed at the study of remotely sensing canopy chemistry using AVIRIS data (Chapter 4). Leaf samples were collected from dominant species on each of 20 50x50m plots. Laboratory analysis of the samples yielded data on nitrogen, lignin, cellulose and water content. Lignin and cellulose concentrations were determined by a sulfuric acid digest method (TAPPI 1975, 1976; Effland 1977; McClaugherty *et al.* 1985; Newman *et al.* 1994). Nitrogen concentrations were determined using the CHN combustion method (Page *et al.* 1982).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

5.2.3 AVIRIS Data

Image data were acquired using NASA's Airborne Visible Infrared Imaging Spectrometer (AVIRIS) on 15 June 1992. AVIRIS records data in 224 contiguous spectral bands covering the spectral range of 0.4 - 2.4μm with a spectral resolution of 10nm. The spatial resolution of this data is 20m with a full scene covering 10x10km (Vane and Goetz 1988).

Atmospheric corrections of the AVIRIS data were done by the **AT**mosphere **REM**oval Program (ATREM) (Gao *et al.* 1991, 1992). This program uses information in each AVIRIS radiance spectra to parameterize a radiative transfer model that is then used to convert the data to ground reflectance by removing the effects of atmospheric gases, water vapor and aerosols. Following the ATREM correction, a secondary correction was made, based on the difference between a ground calibrated scene and an ATREM corrected scene also acquired in 1992 (personal communication K. Heidebrect, R. Clark).

5.2.4 Field Measurement of Species

A geographic information system (GIS) database of species type was obtained from a 1986-1988 stand survey of the study site (Harvard Forest Archive). In this survey, 252 stands within the study site were identified from aerial photos. Basal area by species was measured for each stand using at least 3 variable radius plots located along a transect within each stand. From this data, relative basal area for each species within each stand was calculated. Based on the relative basal area of each species, we placed each stand into one of 11 categories which we then attempted to

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

classify using AVIRIS spectral data (Table 5.1). These categories include stands of pure conifer species (red pine, norway spruce and white pine). With in the study area there were only several stands which contained single hardwood species. These stands were too few and too small to include as separate classification categories.

	Stand Type	Classification Criteria
1	open	no trees
2	hemlock/hardwood	$\geq$ 70% hemlock
3	softwood	$\geq$ 80% mixed softwood
4	norway spruce	$\geq$ 80% norway spruce
5	white pine	$\geq$ 80% white pine
6	red pine	$\geq$ 80% red pine
7	spruce bog	black spruce wetland
8	hardwood bog	wetland with mixed hardwood
9	hardwood	$\geq$ 80% mixed hardwood
10	hardwood/softwood1	26-79% hardwood
11	hardwood/softwood2	$\leq$ 25% hardwood

Table 5.1: Stand classification criteria

Stand data from the Harvard Forest GIS database were geographically registered to the AVIRIS image using global positioning system (GPS) data for the study site and the surrounding area.

5.2.5 Canopy Chemistry Analysis

Multiple linear regression analysis was used to select AVIRIS bands which were closely correlated with field measured canopy chemistry for plots (n=40) located at both Harvard Forest and Blackhawk Island, WI (Chapter 4). The bands selected in this analysis correspond primarily to overtones of mid infrared absorption by molecules within the chemical constituents. Bands in both the visible and near infrared (NIR) regions of the spectra were used in this analysis. Nitrogen con-

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

centrations were predicted with NIR bands centered at 783 and 1641nm. Lignin concentrations were predicted with NIR bands centered at 755, 822 and 1661nm and a visible band at 627nm.

5.2.6 AVIRIS Species Classification

A subset of 11 AVIRIS bands were initially selected for this classification. These bands had been previously used to determine canopy nitrogen and lignin concentration for the study site (Martin and Aber 1993) (Chapter 4).

A supervised classification was done in which 2-8 polygons from each of the 11 categories (total = 47) were used to extract spectral signatures for each class. These polygons were identified using the stand map generated from field data.

Transformed divergence values (ERDAS 1992) were calculated for all combinations of 3, 4, and 5 bands to determine which band combinations would provide the best separablility of signature classes. A maximum likelihood algorithm was used with a first pass parallelepiped classification to assign all pixels in the image into one of the 11 signature classes using the best band subsets. The parallelepiped classification used maximum and minimum values for each signature to determine class assignments (ERDAS 1992).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

5.3 Results and Discussion

5.3.1 Leaf Chemistry and Species Identification

Plots of nitrogen and lignin concentrations for leaves of different species (Figures 5-2 and 5-3) show that neither lignin nor nitrogen concentration alone is sufficient to identify samples by species. However, these data indicate that species identification can be made on the basis of the combined foliar nitrogen *and* lignin information (Figure 5-4). For example, red pine and hemlock have similar nitrogen concentrations but very different lignin concentrations (red pine: 1.11($\pm$0.13) %N, 26.54($\pm$1.29) %lignin; hemlock 1.16($\pm$0.10) %N, 14.82($\pm$0.62) %L), whereas red maple and black cherry have similar lignin concentrations and different nitrogen concentrations (red maple: 1.8($\pm$0.27) %N, 18.04($\pm$1.27) %lignin; black cherry 2.62($\pm$0.26) %N, 17.79($\pm$2.08) %lignin).

5.3.2 AVIRIS Classification of Species

An evaluation of the classifications using the subsets of 3, 4 and 5 bands showed that little to no improvement in classification accuracy occurred with more than 4 bands. The species map generated from the AVIRIS classification (Figure 5-5), uses 4 bands centered at the following wavelengths: 627, 755, 822 and 1641nm. In Chapter 4, the 3 shorter wavelength bands are used in equations predicting foliar lignin concentration, and the band centered at 1641nm is used to predict foliar nitrogen concentration. Samples were selected from the classified image to assess the accuracy of the classification algorithm. 3x3 pixel samples were selected from

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

the center of classified polygons. Approximately 13% of the classified map was used in this accuracy assessment, with the number of samples per class relative to the total area of the class. An error matrix was calculated from the field measured data and AVIRIS classification for these samples (Table 5.2). The diagonal boldface values indicate the number of samples in each class which were correctly classified with AVIRIS data. Producer's and user's accuracy are calculated from this table as described in Congalton (1991) (Tables 5.3 and 5.4). The overall accuracy of the classification is 73.4%, with 127 out of 174 samples correctly classified.

Due to the species composition of the study site, it was impossible to investigate the classification of individual hardwood species - almost all of the hardwood present in this area is a mix of red oak and red maple . Several small stands of pure oak, red maple swamp or sugar maple were identified in the field, however, these were of insufficient size to be used in this supervised classification (4-9 pixels in size).

The only 'pure' species stands that we attempted to separate were conifer stands of hemlock, norway spruce, white pine, red pine and black spruce bog. In the random samples chosen for our accuracy assessment, these species were correctly classified by AVIRIS data in 100, 90, 50, 89 and 87% of the samples, respectively. For most conifer classes, the errors of omission occurred with the other softwood and hardwood/softwood mix classes. Most of the samples in the hardwood/softwood2 class were assigned to one of the conifer categories. In a review of the stand survey data, a number of these pixels were dominated by a single conifer species.

It is important to note that in this analysis we have assumed that relative foliar biomass is proportional to relative basal area. It is likely that this is not true in the

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

mixed hardwood/softwood stands. We know from field sampling of litterfall that a red pine plot with a basal area of $53m^2$/hectare has a foliar biomass of $8488g/ha^2$, whereas a hardwood site with a basal area of $30m^2$/hectare has a foliar biomass of $2540g/ha^2$. In other words, there is nearly twice the foliar biomass per square meter of basal area in the red pine site as in the hardwood site. Since the remotely sensed reflectance spectra is influenced primarily by the foliar biomass, our use of this stand survey data may not be valid for mixed conifer/hardwood stands.

We also validated these predictions against a number of plots in which canopy biomass had been measured by litterfall collections. Litterfall collections were made on 33 plots during 1992 and 1993 within this study site. These plots were in only 4 of the 11 classes described in Table 5.1. The number of these plots correctly classified with AVIRIS data is as follows: hemlock - 1/1; norway spruce - 3/3; hardwood - 19/24; and red pine - 4/5. Three of the five hardwood plots misclassified were assigned to the hardwood/softwood class, one red pine plot was misclassified as hardwood/softwood.

The overall appearance of the AVIRIS classified map shows more spatial heterogeneity than the field classified map. It is possible that small scale spatial variation which might be missed in this type of field survey could be measured by remote sensing data in which spectral data is available for every pixel. The field sampling involved three or more measurements within each stand polygon (with some stands containing several hundred 20x20m pixels).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

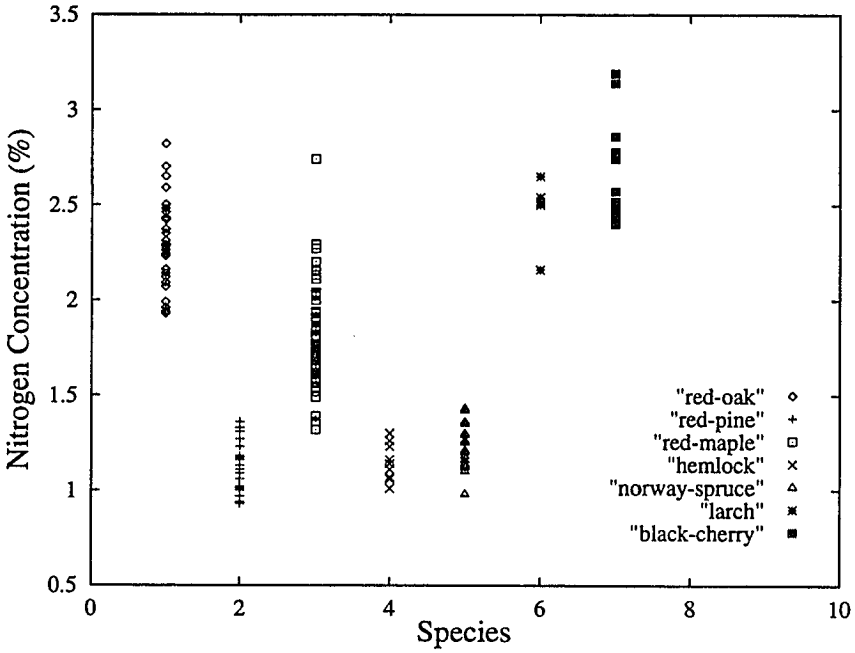


Figure 5-2: Harvard Forest leaf samples: Laboratory measured foliar nitrogen vs species ID

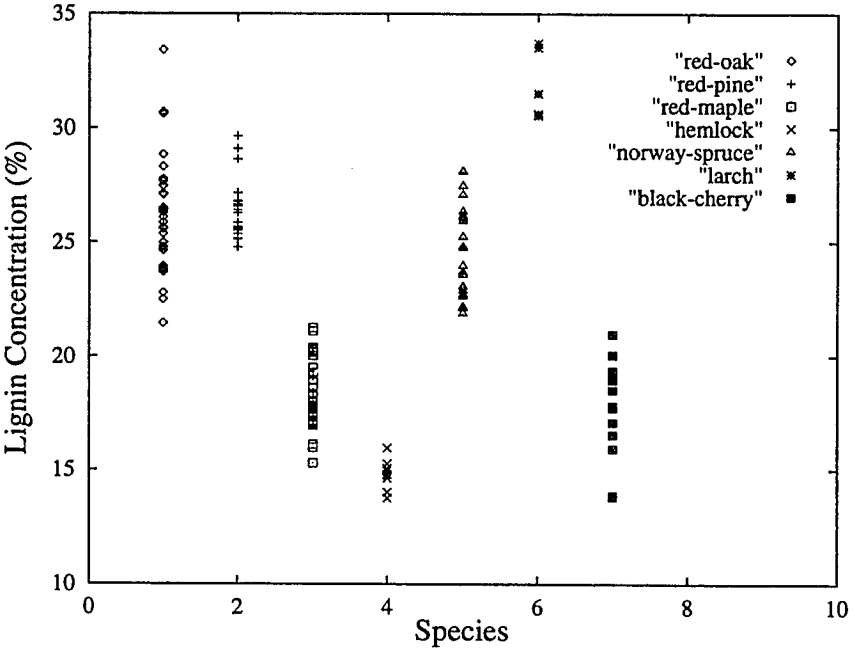


Figure 5-3: Harvard Forest leaf samples: Laboratory measured foliar lignin vs species ID

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

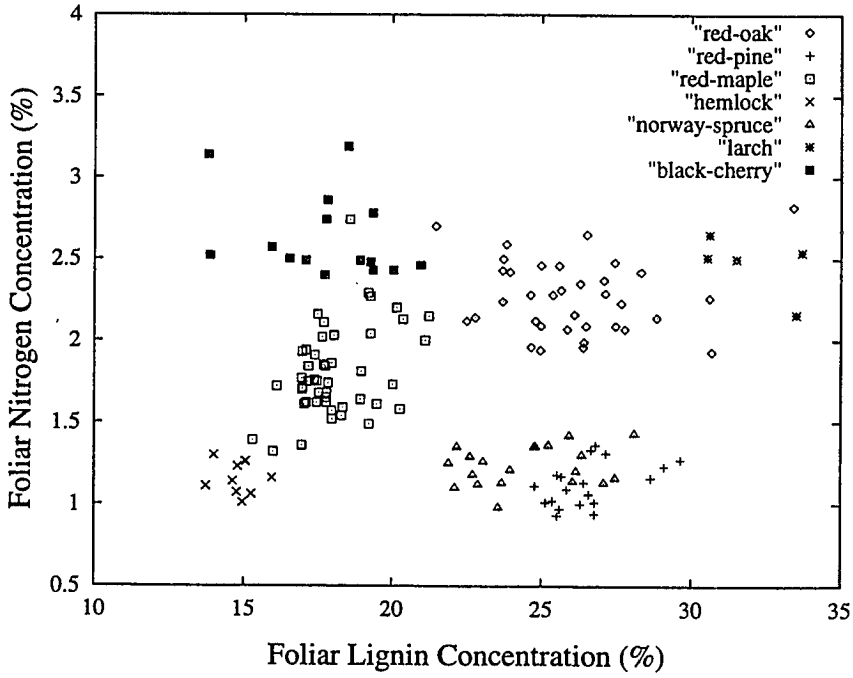


Figure 5-4: Harvard Forest leaf samples: foliar nitrogen vs foliar lignin

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

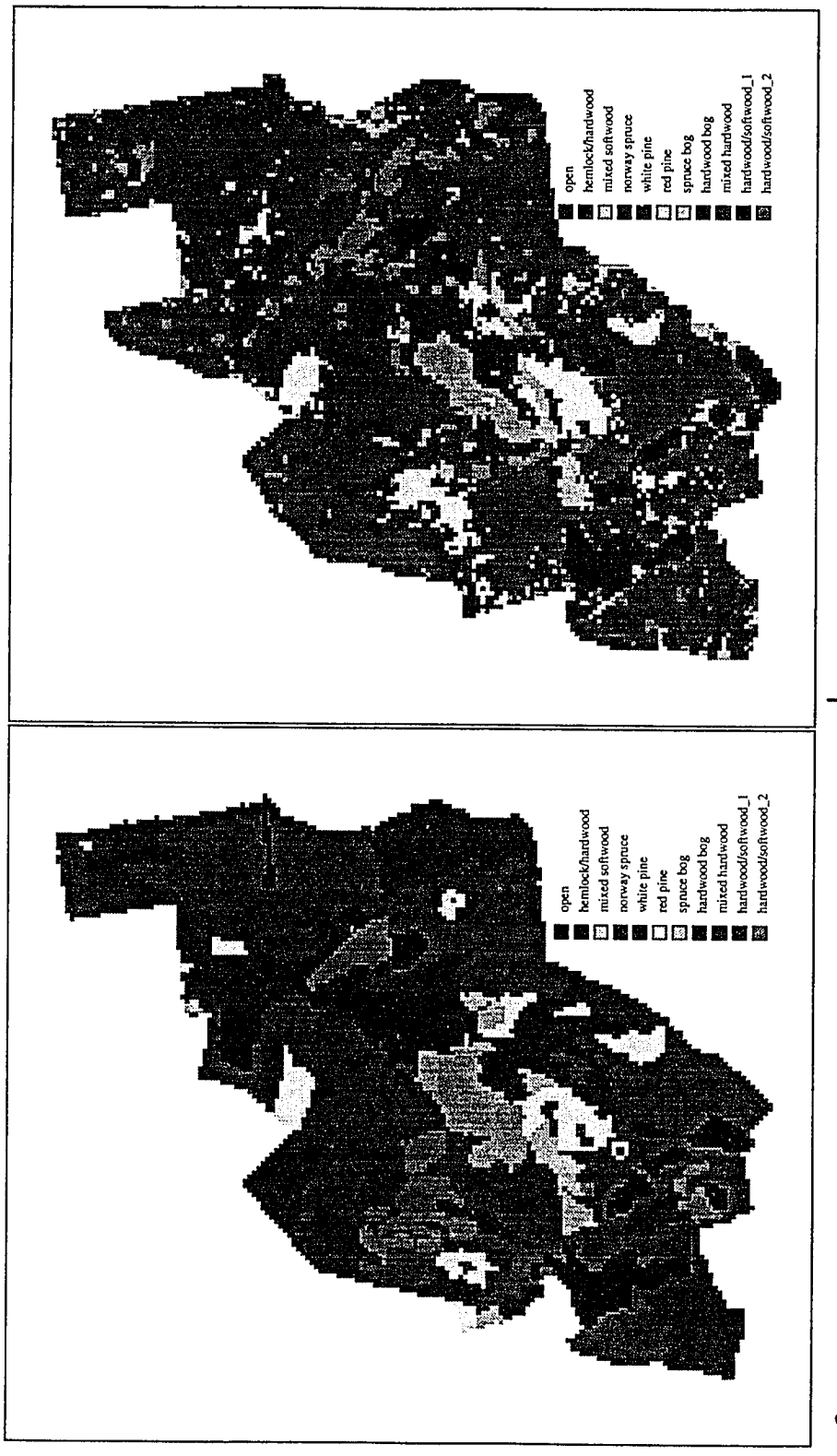


Figure 5-5: Harvard Forest: a. Species stand classification determined from field measurements of basal area. b. Species stand classification from AVIRIS data using bands centered at 627, 755, 822 and 1641nm).

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

		Field Data											
		1	2	3	4	5	6	7	8	9	10	11	row total
AVIRIS Class	1	**12**	0	0	0	0	0	0	0	3	0	0	15
	2	0	**12**	0	0	0	0	1	0	1	2	0	16
	3	0	0	**4**	0	1	0	0	0	0	0	1	6
	4	0	0	0	**9**	0	1	0	0	0	0	1	11
	5	0	0	0	0	**2**	0	0	0	1	1	1	5
	6	0	0	0	1	0	**8**	0	0	0	0	1	10
	7	0	0	0	0	0	0	**7**	0	0	0	0	7
	8	0	0	0	0	0	0	0	**5**	0	0	0	5
	9	0	0	0	0	0	0	0	0	**50**	15	0	65
	10	0	0	0	0	1	0	0	0	9	**16**	0	26
	11	0	0	0	0	0	0	0	1	4	1	**2**	8
	column total	12	12	4	10	4	9	8	6	68	35	6	174

Table 5.2: **Classification error matrix**

Stand Type	Producer's Accuracy		
1	12/12	=	100%
2	12/12	=	100%
3	4/4	=	100%
4	9/10	=	90%
5	2/4	=	50%
6	8/9	=	89%
7	7/8	=	87%
8	5/6	=	83%
9	50/68	=	77%
10	16/35	=	46%
11	2/6	=	33%

Table 5.3: **Producer's accuracy table. Values reported are the number of correctly classified samples in a category divided by the number of samples which were assigned to the category using field data.**

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Stand Type	User's Accuracy		
1	12/15	=	80%
2	12/16	=	75%
3	4/6	=	67%
4	9/11	=	82%
5	2/5	=	40%
6	8/10	=	80%
7	7/7	=	100%
8	5/5	=	100%
9	50/65	=	77%
10	16/26	=	62%
11	2/8	=	25%

Table 5.4: User's accuracy table. Values reported are the number of correctly classified samples in a category divided by the total number of samples which were assigned to the category with the AVIRIS classification.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

5.4 Conclusions

In this work we have used the relationship between foliar chemistry and species identification to demonstrate that high spectral resolution remote sensing data can be used to classify forest species. Remote sensing of canopy chemistry has been possible only in the recent past with the availability of data from such instruments as AVIRIS. Additional work must be done to fully explore the potential of high spectral resolution data in determining forest species composition. Selection of signature training sites based on field measured canopy composition may result in a more accurate classification, particularly in mixed hardwood/softwood stands. Improvements may also be made in the classification of hardwood/softwood mixed stands by first using leaf on/leaf off data to determine the foliar biomass proportion of each type before attempting species classification.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Chapter 6

CONCLUSIONS

A current goal in remote sensing technology and data analysis is to successfully measure forest foliar chemistry. Since foliar chemistry is closely tied to a number of ecosystem processes, accomplishment of this goal will provide the necessary tools to make regional and global estimates of carbon and nutrient cycling in forest ecosystems, and to determine the spatial variability of these processes. In Chapter 3 we describe an analysis involving the laboratory spectra of fresh whole leaves in an effort to bridge the gap between the spectral analysis of dried ground leaves and the spectral analysis of whole canopies via remote sensing. The results of this work indicate that, although there is strong water absorption throughout the NIR spectra, information on the biochemical content of foliage is present in the laboratory spectra of fresh leaves. The wavelengths most successfully used in this analysis were different than those used in the analysis of dried ground leaves due to the strong absorption by water in two regions of the infrared spectrum. It is difficult to apply these results directly to the spectra obtained by AVIRIS because of differences in data quality (signal:noise) between the two instruments. In the fresh leaf NIR analysis of nitrogen and lignin a number of the bands used were $\geq$ 2000nm. Unfortunately, the data acquired from AVIRIS has the lowest signal:noise in this spectral region. AVIRIS also covers a wider spectral region than the laboratory instrument

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

used in this study; 400-2500nm vs 1100-2500nm. Further laboratory analysis with a broader spectrum instrument may provide additional insight into the use of AVIRIS data in the remote sensing of canopy chemistry.

The analysis of AVIRIS data to determine canopy lignin and nitrogen concentration, described in Chapter 4, suggests that spectral measurements at the whole canopy level also contain information adequate for the determination of foliar biochemistry. We found strong correlations between AVIRIS data and field measured nitrogen and lignin concentrations comparable to the correlations observed at the fresh leaf level. Predictions of canopy nitrogen and lignin concentrations were valid only when data points within the same AVIRIS dataset were used to develop the calibration equations. This indicates that geographic or atmospheric differences in remotely sensed imagery may make the development of generalizable equations difficult. Spectral sensitivity to atmospheric conditions, and the process of removing these effects will be the subject of continuing study.

In addition to measuring canopy nitrogen and lignin concentrations at both Harvard Forest and Blackhawk Island, we used these spatial estimates to drive ecosystem models predicting nitrogen mineralization rates and carbon balance. Prior to the nitrogen driven PnET model output, estimates of carbon balance at Harvard Forest had been made with the model using only a single set of input variables which attempted to describe the entire study site. The addition of the spatial dimension to a model such as this, increases the accuracy of carbon balance predictions over those made with spatially averaged input variables. Nitrogen mineralization values at Blackhawk Island were predicted using AVIRIS derived canopy lignin and a pre-

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

viously established relationship between canopy lignin and nitrogen mineralization.

An analysis of leaf samples collected from the study sites revealed that foliar nitrogen and lignin concentrations could be used to identify samples by species. Using the results from the canopy chemistry analysis, we were able to use selected AVIRIS bands to identify a number of species classes at the Harvard Forest. Improvements in AVIRIS species classification may be obtained by resampling field sites, measuring canopy species distribution rather than basal area.

At the present time, high spectral resolution imaging data is available from only a few instruments (e.g. AVIRIS). High spectral resolution remote sensing instruments provide the data to make measurement of forest canopy characteristics which could not be made with broad band sensors. Continuing analysis of this data will determine the role that such instruments will have in satellite and airborne programs directed at the study of the earth.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

REFERENCES

Aber, J. D. and Federer, C. A. (1992). A generalized, lumped-parameter model of photosynthesis, evapotranspiration and net primary production in temperate and boreal forest ecosystems. *Oecologia*, **92**, 463–474.

Aber, J. D. and Melillo, J. M. (1982). Nitrogen immobilization in decaying hardwood leaf litter as a function of initial nitrogen and lignin content. *Canadian Journal of Botany*, **60**, 2263–2269.

Aber, J. D. and Melillo, J. M. (1991). *Terrestrial Ecosystems.* Saunders College Publishing, Philadelphia.

Aber, J. D., Melillo, J. M., and McClaugherty, C. A. (1990). Predicting long-term patterns of mass loss, nitrogen dynamics, and soil organic matter formation from initial fine litter chemistry in temperate forest ecosystems. *Canadian Journal of Botany*, **68**, 2201–2208.

Aber, J. D., Magill, A., Boone, R., Melillo, J. M., Steudler, P., and Bowden, R. (1993). Plant and soil responses to chronic nitrogen additions at the Harvard Forest, Massachusetts. *Ecological Applications*, **3**, 156–166.

Abrams, S. M., Shenk, J. S., and Harpster, W. H. (1988). Potential of near infrared reflectance spectroscopy for analysis of silage composition. *Journal of Dairy Science*, **71**, 1955–1959.

Barton II, F. (1987). Analytical application to fibrous foods and commodities. In *Near-Infrared Technology in the Agricultural and Food Industries*, pages 169–184. American Association of Cereal Chemists, Inc, St. Paul, Minnesota, USA.

Barton II, F. E. and Windham, W. R. (1988). Determination of acid-detergent fiber and crude protein in forages by near-infared reflectance spectroscopy: collaborative study. *Journal Association Official Analytical Chemistry*, **71**.

Barton II, F. E., Himmelsbach, D., Duckworth, J., and Smith, M. J. (1992). Two-dimensional vibration spectroscopy: Correlation of mid- and near-infrared. *Applied Spectrocopy*, **46**.

Berg, B., Ekbohm, G., and McClaugherty, C. (1984). Lignin and holocellulose relations during long-term decomposition of some forest litters. Long-term decomposition in a scots pine forest. IV. *Canadian Journal of Botany*, **62**, 2540–2550.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Bowden, R. D., Steudler, P. A., Melillo, J. M., and Aber, J. D. (1991). Annual nitrous oxide fluxes from temperate forest soils in the northeastern United States. *Journal of Geophysical Research*, **96**, 13997–14005.

Bradshaw, A. and McNeilly, T. (1991). Evolutionary response to global climatic change. *Annals of Botany*, **Supplement 1**, 4–15.

Card, D. H., Peterson, D. L., and Matson, P. A. (1988). Prediction of leaf chemistry by the use of visible and near infrared reflectance spectroscopy. *Remote Sensing of Environment*, **26**, 123–147.

Casciero, J. L. and DiGiovanni, E. J. (1985). *Compscan Systems: Theory Manual.* Pacific Scientific Company.

Chapin III, F. S. and Kedrowski, R. A. (1983). Seasonal changes in nitrogen and phosphorus fractions and autumn retranslocation in evergreen and deciduous taiga trees. *Ecology*, **64**, 376–391.

Clark, R. N., Swayze, G., Heidebrecht, K., Goetz, A. F. H., and Green, R. O. (1993). Comparison of methods for calibrating AVIRIS data to ground reflectance. In R. O. Green, editor, *Summaries of the Fourth Annual JPL Airborne Geoscience Workshop: AVIRIS*, volume 1, pages 35–36. Jet Propulsion Laboratory.

Computing Resource Center (1992). *STATA Reference Manual: Release 3. 5th ed.* Computing Resource Center, Santa Monica, CA.

Congalton, R. G. (1991). A review of assessing the accuracy of classifications of remotely sensed data. *Remote Sensing of Environment*, **37**, 35–46.

Cramer, W. and Leemans, R. (1993). Assessing impacts of climate change on vegetation using climate classification systems. In A. M. Solomon and H. H. Shugart, editors, *Vegetation Dynamics and Global Change.* Chapman and Hall, New York.

Curran, P. J. (1989). Remote sensing of foliar chemistry. *Remote Sensing of Environment*, **30**, 271–278.

Daubenmire, R. and Prusso, D. C. (1963). Studies of the decomposition rates of tree litter. *Ecology*, **44**(3), 589–592.

Davis, M., Woods, K., Webb, S., and Futyama, R. (1986). Dispersal versus climate: expansion of *Fagus* and *Tsuga* into the Upper Great Lakes region. *Vegetatio*, **67**, 93–103.

Dixit, L. and Ram, S. (1985). Quantitative analysis by derivative electronic spectroscopy. *Applied Spectroscopy Reviews*, **21**, 311–418.

Effland, M. (1977). Modified procedure to determine acid insoluble lignin in wood and pulp. *Tappi*, **60**(10), 143–144.

Elvidge, C. D. (1988). Vegetation reflectance features in AVIRIS data. In *International symposium on remote sensing of environment, ERIM*, pages 169–182, Houston, Texas. ERIM.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

ERDAS (1992). *ERDAS Field Guide.* ERDAS, Inc, Atlanta, GA.

Everitt, J., Escobar, D., Alaniz, M., and Davis, M. (1987). Using airborne middle-infrared (1.45-2.0μm) video imagery for distinguishing plant species and soil conditions. *Remote Sensing of Environment*, **22**, 423–428.

Field, C. and Mooney, H. A. (1986). *The photosynthesis-nitrogen relationship in wild plants*, pages 25–55. Cambridge University Press.

Fogel, R. and Cromack, K. (1976). Effect of habitat and substrate quality on douglas fir litter decomposition in western Oregon. *Canadian Journal of Botany*, **55**, 1632–1640.

Gao, B., Goetz, A. F. H., and Zamudio, J. (1991). Removing atmospheric effects from AVIRIS data for surface reflectance retrievals. In R. O. Green, editor, *Proceedings of the Third Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) Workshop*, pages 80–86. Jet Propulsion Lab.

Gao, B., Heidebrecht, K., and Goetz, A. F. H. (1992). *Atmosphere removal program (ATREM) user's guide.* Center for the Study of Earth from Space/CIRES, University of Colorado.

Gates, D. M., Keegan, H. J., Schleter, J. C., and Weidner, V. R. (1965). Spectral properties of plants. *Applied Optics*, **4**, 11–20.

Goetz, A. F., Vane, G., Solomon, J. E., and Rock, B. N. (1985). Imaging spectrometry for earth remote sensing. *Science*, **228**, 1147–1153.

Halliday, D. and Resnick, R. (1986). *Fundamentals of Physics.* John Wiley and Sons, New York.

Himmelsbach, D., Boer, H., Akin, D., and Barton II, F. (1988). Solid-state 13C NMR, FTIR, and NIRS spectroscopic studies of ruminant silage digestion. In *Analytical Applications of Spectroscopy.* Royal Society of Chemistry, Cambridge.

Hodgson, M., Jensen, J., Mackey Jr, J., and Coulter, M. (1988). Monitoring wood stork foraging habitat using remote sensing and geographic information systems. *Photogrammetric Engineering and Remote Sensing*, **54**, 1601–1607.

Hrushcka, W. R. (1987). Data analysis: Wavelength selection methods. In P. Williams and K. Norris, editors, *Near-Infrared Technology in the Agricultural and Food Industries.* American Association of Cereal Chemists, Inc, St. Paul, Minnesota, USA.

Johnson, L., Hlavka, C. A., and Peterson, D. L. (1994). Multivariate analysis of AVIRIS data for canopy biochemical estimation along the Oregon transect. *Remote Sensing of Environment*, **47**, 216–230.

Johnson, L. F. and Peterson, D. L. (1991). AVIRIS observation of forest ecosystems along the Oregon transect. In R. O. Green, editor, *Proceedings of the Third Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) Workshop*, pages 190–199. Jet Propulsion Lab.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Lathrop, R. G., Aber, J., Bognar, J. A., Ollinger, S., Casset, S., and Ellis, J. M. (1994). GIS development to support regional simulation modeling of northeastern (USA) froest ecosystems. In W. Michener, J. W. Brunt, and S. Stafford, editors, *Environmental Information Magnagement and Analysis.* Taylor and Francis Publishers, London.

Lindberg, W., Persson, J., and Wold, S. (1983). Partial least-squares method for spectroflourimetric analysis of mixtures of humic acid and ligninsulfonate. *Analytical Chemistry*, **55**(4), 643–648.

Lindberg, W., Ohman, J., Wold, S., and Martens, H. (1985). Simultaneous determination of five different food proteins by high-performance liquid chromotography and partial least-squares multivariate calibration. *Analytica Chimica Acta*, **174**, 41–51.

MacLean, K. and Robertson, R. (1981). Variation in the major element content of red spruce foliage with season, crown position, tree and tissue age. *Communications in Soil Science and Plant Analysis*, **12**, 39–491.

Mark, H. and Workman, J. (1991). *Statistics in Spectroscopy.* Academic Press, San Diego.

Marten, G., Shenk, J., and Barton II, F. E. (1989). Near infrared reflectance spectroscopy (NIRS): Analysis of forage quality. Technical Report 643, United States Department of Agriculture.

Martin, A. (1966). *Infrared Instrumentation and Techniques.* Elsevier Publishing Comapany, Amsterdam.

Martin, M. and Aber, J. (1990). Effects of moisture content and chemical composition on the near infrared spectra of forest foliage. In *Imaging Spectroscopy of the Terrestrial Environment*, Orlando, FL. SPIE.

Martin, M. and Aber, J. (1993). Measurements of canopy chemistry with 1992 AVIRIS data at Blackhawk Island and Harvard Forest. In R. O. Green, editor, *Summaries of the Fourth Annual JPL Airborne Geoscience Workshop: AVIRIS*, volume 1, pages 113–116. Jet Propulsion Laboratory.

Matson, P., Johnson, L., Billow, C., Miller, J., and Pu, R. (1994). Seasonal patterns and remote spectral estimation of canopy chemistry across the Oregon transect. *Ecological Applications*, **4**, 280–298.

McClaugherty, C. and Berg, B. (1987). Cellulose, lignin and nitrogen concentrations as rate regulating factors in late stages of forest litter decomposition. *Pedobiologia*, **30**, 101–112.

McClaugherty, C. A., Pastor, J., Aber, J. D., and Melillo, J. M. (1985). Forest litter decomposition in relation to soil nitrogen dynamics and litter quality. *Ecology*, **66**, 266–275.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

McLellan, T., Martin, M. E., Aber, J. D., Melillo, J. M., Nadelhoffer, K. J., and Dewey, B. (1991a). Comparison of wet chemical and near infrared reflectance measurements of carbon fraction chemistry and nitrogen concentration of forest foliage. *Canadian Journal of Forestry*, **21**, 1689–1693.

McLellan, T. M., Aber, J. D., Martin, M. E., Melillo, J. M., and Nadelhoffer, K. J. (1991b). Determination of nitrogen, lignin, cellulose content of decomposing leaf material by near infrared reflectance spectroscopy. *Canadian Journal of Forestry*, **21**, 1684–1688.

Meentemeyer, V. (1978). Macroclimate and lignin control of litter decompostition rates. *Ecology*, **59**, 465–472.

Melillo, J. M., Aber, J. D., and Muratore, J. F. (1982). Nitrogen and lignin control of hardwood leaf litter decomposition dynamics. *Ecol.*, **63**, 621–626.

Mooney, H., Vitousek, P., and Matson, P. (1987). Exchange of materials between terrestrial ecosystems and the atmosphere. *Science*, **238**, 926–932.

Murray, I. and Williams, P. (1987). Chemical principles of near-infrared technology. In P. Williams and K. Norris, editors, *Near-Infrared Technology in the Agricultural and Food Industries*. American Association of Cereal Chemists, Inc, St. Paul, Minnesota, USA.

Nadelhoffer, K. J., Aber, J. D., and Melillo, J. M. (1982). Leaf-litter production and soil organic matter dynamics along a nitrogen-availability gradient in Southern Wisconsin (USA). *Canadian Journal of Forest Research*, **13**, 12–21.

Nelson, R., Latty, R. S., and Mott, G. (1985). Classifying northern forests using Thematic Mapper Simulator data. *Photogrammetric Engineering and Remote Sensing*, **50**, 607–617.

Newman, S. D., Soulia, M., and Aber, J. D. (1994). Proximate carbon freaction an nitrogen analyses for the Accelerated Canopy Chemistry Program: Methods and quality control.

Norris, K. H., Barnes, R. F., Moore, J. E., and Shenk, J. S. (1976). Predicting forage quality by infrared reflectance spectroscopy. *Journal of Animal Science*, **43**, 889–897.

Olson, J. (1963). Energy storage and the balance of producers and decomposers in ecological systems. *Ecology*, **44**, 322–331.

Osborne, B. and Fearn, T. (1986). *Near Infrared Spectroscopy in Food Analysis*. Longman Scientific and Technical Publishing Co.

Page, A. L., Miller, R. H., and Keeney, D., editors (1982). *Methods of Soil Analysis*, volume 2. American Society of Agronomy, Inc, Madison, WI.

Pastor, J., Aber, J. D., McClaugherty, C. A., and Melillo, J. M. (1982). Geology, soils and vegetation of Blackhawk Island, Wisconsin. *American Midland Naturalist*, **108**, 266–277.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Pastor, J., Aber, J. D., McClaugherty, C. A., and Melillo, J. M. (1984). Aboveground production and N and P cycling along a nitrogen mineralization gradient on Blackhawk Island, Wisconsin. *Ecology*, **65**, 256–268.

Peterson, D. L. and Waring, R. H. (1993). Overview of the Oregon transect ecosystem research project. *Ecological Applications*, **4**, 211–225.

Peterson, D. L., Aber, J. D., Matson, P. A., Card, D. H., Swanberg, N., Wessman, C., and Spanner, M. (1988). Remote sensing of forest canopy and leaf biochemical contents. *Remote Sensing of Environment*, **24**, 85–108.

Porter, W. M. and Enmark, H. T. (1987). A system overview of the Airborne Visible/Infrared Imaging Spectrometer (AVIRIS). In G. Vane, editor, *Imaging Spectroscopy II*, pages 22–31. The International Society for Optical Engineers.

Reich, P. B., Walters, M. B., and Ellsworth, D. S. (1991). Leaf age and season influence the relationships between leaf nitrogen, leaf mass per area and photosynthesis in maple and oak trees. *Plant, Cell and Environment*, **14**, 251–259.

Reich, P. B., Walters, M. B., and Ellsworth, D. S. (1992). Leaf life-span in relation to leaf, plant, and stand characteristics among diverse ecosystems. *Ecological Monographs*, **62**, 365–392.

Reimer, J., Heyada, J., Carpenter, S., Deich, W., and Lee, M. (1987). AVIRIS ground data-processing system. In *Imaging Spectroscopy II*, San Diego, CA. SPIE.

Rock, B., Hoshizake, T., and Miller, J. (1988). Comparison of in situ and airborne spectral measurements of the blue shift associated with forest decline. *Remote Sensing of Environment*, **24**, 109–127.

Rock, B. N., Williams, D. L., Moss, D. M., Lauten, G. N., and Kim, M. (1994). High-spectral resolution field and laboratory optical reflectance measurements of red spruce and eastern hemlock needles and branches. *Remote Sensing of Environment*, **47**, 176–189.

Rohde, W. and Olson Jr, C. (1972). Multispectral sensing of forest tree species. *Photogrammetric Engineering and Remote Sensing*, **38**, 1209–1215.

Schaefer, D., Steinberger, Y., and Whitford, W. G. (1985). The failure of nitrogen and lignin control of decomposition in a North American desert. *Oecologia*, **65**, 382–386.

Shen, S., Badhwar, G., and Carnes, J. (1985). Separability of boreal forest species in the Lake Jennette area, Minnesota. *Photogrammetric Engineering and Remote Sensing*, **51**, 1775–1783.

Shenk, J. S., Westerhaus, M. O., and Hoover, M. R. (1979). Analysis of forages by infrared reflectance. *Journal of Dairy Science*, **62**, 807–812.

Shenk, J. S., Landa, I., Hoover, M. R., and Westerhaus, M. O. (1981). Description and evaluation of a near infrared reflectance spectro-computer for forage and grain analysis. *Crop Science*, **21**, 355–358.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Sjostrom, M., Wold, S., Lindberg, W., Persson, J., and Martens, H. (1983). A multivariate calibration problem in analytical chemistry solved by partial least-squares models in latent variables. *Analytica Chimica Acta*, **150**, 61–70.

Skidmore, A. (1989). An expert system classifies eucalypt forest types using Thematic Mapper data and a digital terrain model. *Photogrammetric Engineering and Remote Sensing*, **55**, 1449–1464.

Solomon, A. M. and Cramer, W. (1993). Biospheric implications of global environmental change. In A. M. Solomon and H. H. Shugart, editors, *Vegetation Dynamics and Global Change*. Chapman and Hall, New York.

Staaf, H. and Stjernquist, I. (1986). Seasonal dynamics, especially autumnal retranslocation, of nitrogen and phosphorus in foliage of dominant and suppressed trees of beech, *Fagus sylvatica*. *Scandanavian Journal of Forest Research*, **1**, 333–342.

Steudler, P., Bowden, R., Melillo, J. M., and Aber, J. (1989). Influence of nitrogen fertilization on methane uptake in temperate forest soils. *Nature*, **341**, 314–316.

TAPPI (1975). *Water Solubles in wood an pulp*. Technical Association of the Pulp and Paper Industry, Atlanta, GA.

TAPPI (1976). *Alcohol-benzene and dichloromethane soluble in wood and pulp*. Technical Association of the Pulp and Paper Industry, Atlanta, GA.

Upadhyay, V., Singh, J., and Meentemeyer, V. (1989). Dynamics and weight loss of leaf litter in central Himalayan forests: abiotic versus litter quality influences. *Journal of Ecology*, **77**, 147–161.

Vane, G. and Goetz, A. F. H. (1988). Terrestrial imaging spectroscopy. *Remote Sensing of Environment*, **24**, 1–29.

Vane, G., Porter, W. M., Reimer, J. H., Chrien, T., and Green, R. (1988). AVIRIS perfomance during the 1987 flight season: An AVIRIS project assessment and summary of the NASA-sponsored performance evaluation. In G. Vane, editor, *Proceedings of the Airborne Visible/Infrared Imaging Spectrometer (AVIRIS) Performance Evaluation Workshop*, pages 1–20. Jet Propulsion Lab.

Wessman, C. A. (1990). Evaluation of canopy biochemistry. In R. Hobbs and H. A. Mooney, editors, *Remote Sensing of Biosphere Funcioning*, pages 135–156. Springer-Verlag.

Wessman, C. A., Aber, J. D., Peterson, D. L., and Melillo, J. M. (1988a). Foliar analysis using near infrared reflectance spectroscopy. *Canadian Journal of Forest Research*, **18**, 6–11.

Wessman, C. A., Aber, J. D., Peterson, D. L., and Melillo, J. M. (1988b). Remote sensing of canopy chemistry and nitrogen cycling in temperate forest ecosystems. *Nature*, **335**, 154–156.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Wessman, C. A., Aber, J. D., and Peterson, D. L. (1989). An evaluation of imaging spectrometry for estimating forest canopy chemistry. *International Journal of Remote Sensing*, **10**, 1293–1316.

Weyer, L. (1985). Near-infrared spectroscopy of organic substances. *Applied Spectroscopy Reviews*, **21**, 1–43.

White, D. L., Haines, B. L., and Boring, L. R. (1988). Litter decomposition in southern Appalachian black locust and pine-hardwood stands: litter quality and nitrogen dynamics. *Canadian Journal of Forest Research*, **18**, 54–63.

Williams, P. C. and Norris, K. (1987). *Near-Infrared Technology in the Agricultural and Food Industries.* American Association of Cereal Chemists, Inc, St. Paul, Minnesota, USA.

Williams, P. C., Preston, K. R., Norris, K. H., and Starkey, P. M. (1984). Determination of amino acids in wheat and barley by near-infrared reflectance spectroscopy. *Journal of Food Science*, **49**, 17–20.

Williams, P. C., Norris, K., and Sobering, D. C. (1985). Determination of protein and moisture in wheat and barley by near-infrared transmission. *Journal of Agricultural and Food Chemistry*, **33**, 239–244.

Wofsy, S. C., Goulden, M. L., Munger, J. W., Fan, S. M., Bakwin, P., Daube, B., Bassow, S., and Bazzaz, F. A. (1993). Net exchange of CO2 in a mid-latitude forest. *Science*, **260**, 1314–1317.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.